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SOUTH AFRICAN FISH POISONOUS PLANTS

PART III—PRELIMINARY CHEMICAL INVESTIGATION OF THE TUBER OF *NEORAUTANENIA FICIFOLIA* C.A.SM.

by

N. SAVAGE and P. W. G. GROENEWOUD

OPSOMMING

Sewe organiese verbindings en rotenoon is uit die bol van die Suid Afrikaanse plant, *Neorautanenia ficifolia* C.A.Sm., geisoleer. Hierdie verbindings is ontleed en voorlopige molekulere formules word aangedui. Twee van hierdie stowwe is ook uit Neorautanenia edulis verkry. Die toksisiteit van hierdie verbindings is ondersoek en drie se toksisiteitskurwes is opgestel en met die van rotenoon vergelyk. Die toksisiteit van die drie verbindings is heelwat laer as die van rotenoon.

SUMMARY

Seven substances have been isolated from the tuber of *Neorautanenia ficifolia* C.A.Sm., a South African plant, while rotenone has been obtained in a small-scale preliminary examination of the tuber. From analytical data molecular formulae have been tentatively suggested. Two of these substances were previously isolated from Neorautanenia edulis. Three of them have been found to be fish toxic Their toxicity curves have been constructed and compared with that of rotenone showing that they are less toxic than rotenone.

Both the aerial portion and the tuber of the plant *Neorautanenia ficifolia* C.A.Sm. occurring in Eastern South Africa, are known to be toxic to fish. The plant has also been reported to possess insecticidal activity.

The purpose of this investigation was to attempt the isolation of the toxic principles contained in the tuber of the plant.

Preliminary experiments were carried out on a small amount of plant material collected near The Fountains, Pretoria, during the month of November. Since in the course of these experiments a small amount of rotenone was isolated together with other crystalline material, it was suspected that the toxic principles present probably belonged to the rotenone group of fish poisons. A larger amount of the tuber was therefore extracted by cold percolation with ether. The material used in this work was collected near Rietvlei, about 12 miles south of Pretoria, during the month of February. The extracts obtained from this material did not yield any rotenone whatsoever, a fact which is very likely due to a seasonal variation in the plant itself; this, however, has not yet been thoroughly investigated.

METHODS

The extraction to exhaustion of the ground tuber by percolation with ether, gave rise to the two following main fractions:

Fraction A—a mustard coloured crystalline material which separated from the concentrated ethereal solution on standing.

Fraction B—a dark brown residue obtained from the filtered ethereal solution by evaporation.

These fractions were examined separately.

Fraction A

The substances present in this fraction showed very similar solubility in the common solvents and were therefore best separated by chromatographic adsorption on activated alumina, first from dichloroethane as solvent, followed by further separation with 1,2-dichlorethylene. Acetone proved the most satisfactory eluent for the less strongly adsorbed bands, whilst a mixture of acetone and methyl alcohol was necessary to elute the more strongly adsorbed bands.

The above method, applied in a large-scale separation of Fraction A, led to the isolation of the following substances:

Substance (i) —white, amorphous powder, m.p. 136°C.
Substance (ii) —yellow needles, m.p. 211°C.
Substance (iii)—yellow prisms, m.p. 180°C.
Substance (iv)—pale-yellow, rod-like needles, m.p. 197°C.

Fraction B

A very effective preliminary purification was accomplished by adsorption of the greater part of the resinous material on activated alumina from acetone as solvent. From the purified material the following crystalline substances were isolated, in addition to substances (ii) and (iii):

Substance (v) —colourless, short prisms, m.p. 181·5°C.
Substance (vi)—colourless, shiny flakes, m.p. 160°C.

Since certain toxic materials, present in plants of the Derris type, are known to be isolated from non-crystalline extracts only after treatment with alkali,[1 2 3] a portion of Fraction B was subjected to a similar treatment prior to chromatographic analysis. It appeared however that this procedure did not result in the isolation of any new substances, although it did facilitate the isolation of some of the above-mentioned crystalline products.

During the preliminary small-scale extraction of the tuber, a bright yellow crystalline material, m.p. 193·5°C, was isolated as very fine needles. This substance like rotenone, could not again be isolated from subsequent extracts. It was however investigated with the others and will be referred to as substance (vii).

Of the above crystalline products, (ii) and (iii)) were recognised, by a determination of mixed melting points with authentic specimens, as substances previously isolated from *Neorautanenia edulis*[4]. The remaining substances were found to be free from nitrogen, the halogens and sulphur and were therefore analysed for carbon and hydrogen (analyses by Dr. Weiler, Oxford, England) and their molecular weights determined by the depression of the melting point of pure camphor. From the analytical values obtained, the following molecular formulae are tentatively suggested:

Substance (i) —$C_{13}H_{26}O_2$
Substance (ii) —$C_{18}H_{12}O_6$[4]
Substance (iii) —$C_{19}H_{14}O_6$[4]
Substance (iv) —$C_{16}H_{12}O_6$
Substance (v) —$C_{22}H_{14}O_7$
Substance (vi) —$C_{18}H_{30}O$
Substance (vii)—$C_{17}H_{12}O_6$

No further definite information regarding the identity or molecular structure of these substances is yet available. Work in this connection and on further suspected toxic materials which may be present is in progress and will be reported later. From their general properties, molecular weights and molecular formulae it must be concluded that they are in no way related to the rotenone group of fish poisons.

FISH-TOXIC PROPERTIES OF THE CRYSTALLINE MATERIALS

In examining the fish-toxic properties of the isolated substances, the procedures previously described[4] had to be used, because of the negligible solubility of the pure materials in aerated distilled water. Control tests proved that the reagents, viz. gelatine and acetone, at suitable concentrations, had no ill-effects on Lebistes reticulatus, a type of fresh-water fish used for toxicity determination.

Of the substances isolated, the following three were found to be toxic to fish:
Substance (iii) —$C_{19}H_{14}O_6$, m.p. 180°C.
Substance (v) —$C_{22}H_{14}O_7$, m.p. 181·5°C.
Substance (vii)—$C_{17}H_{12}O_6$, m.p. 193·5°C.

The toxicity curves for these three substances, as well as for rotenone, were constructed under identical experimental conditions and the minimum survival times in minutes were found to be 19 for rotenone, about 44 for substance (iii), 47 for substance (vii) and 60 for substance (v). This means that at higher concentrations substances (iii) and (vii) are nearly equally toxic, substance (v) a little less so and rotenone is considerably more toxic than all three.

The velocity of fatality curves for substances (iii), (v), (vii) and rotenone were constructed and are shown in Figs. 1, 2, 3 and 4 respectively. From these curves the thresholds of toxicity (i.e. the concentrations, expressed as m.g./litre, below which the substances do not cause death) were found to be 0·9 for substance (iii), 1·15 for substance (v), 0·6 for substance (vii) and 0·04 for rotenone. Toxicity therefore decreases in the order rotenone > substance (vii) > substance (iii) > substance (v). If the rate of increase of velocity of fatality with increase in concentration (obtained from the slope of that portion of the curve that approaches a straight line) be regarded as the criterion of toxicity, the latter is seen to decrease in the same order as given above.

EXPERIMENTAL

All melting points are corrected.

Preliminary Extraction

A small amount of the tuber was ground and extracted by cold percolation with ether. The solvent was distilled from the solution leaving a brown resinous residue. This was purified by dissolution in ethyl acetate, the solution being passed twice through a column of activated alumina. The residue obtained from this solution on evaporation, was extracted four times with small amounts of ether, giving a yellow solution and an insoluble residue.

The ethereal solution on concentration and standing deposited a yellow oil and crystals formed on the sides of the container. The crystals were identified as rotenone by taking mixed melting points with an authentic specimen.

The insoluble residue was extracted with methyl alcohol and the yellow solution deposited crystals on evaporation. These were dissolved in dichloroethane and by chromatography on activated alumina, a yellow crystalline material—substance (vii)—was obtained, which crystallised from a mixture of chloroform and ethyl alcohol in bright yellow needles, m.p. 193·3°C.

Found: C, 65·82%; H, 3·64%; Molecular weight 314.

$C_{17}H_{12}O_6$ requires: C, 65·37%; H, 3·85%; Molecular weight 312.

Method of Large-scale Extraction

The moist tubers as received were cut into small pieces, dried in air and finally pulverised to yield 12 kg. of powdered material, which was slowly percolated with ether in a copper percolater until extraction was complete. The greater part of the solvent was removed from the extract by distillation and the concentrate on standing deposited some crude crystalline material, which was removed by filtration. (Yield = 37 g. Fraction A.)

Evaporation of the filtrate left a dark brown resinous mass which finally dried to form a brittle product. (Yield = 220 g. Fraction B.)

Separation, Isolation and Purification

Fraction A. 2 g. portions of the crude crystalline material were disolved in 30 ml. dichloroethane and the solution brought onto a column of activated alumina (67 × 1·5 cm.). The chromatogram was developed with the same solvent until a maximum separation of bands had been obtained. The column was extruded and cut into the following four fractions, corresponding to the developed bands:

Bands	*Colour*	*Section of Column*
AI	Dark brown	Top
AII	Orange	
AIII	Light yellow	
AIV	Dark yellow	Bottom

6 g. of fraction A were thus treated.

Fraction AI. This fraction was eluted by extraction in a Soxhlet for six hours with a mixture of acetone and methyl alcohol. The dark brown resinous extract, on standing, deposited some material which was removed by filtration. The filtrate was decolorised by boiling twice with norite and most of the solvent removed. On standing, the residual solution deposited a durther amount of the above material. The combined yield was repeatedly recrystallised from methyl alcohol to give substance (i), m.p. 136°C. Further recrystallisation, also from other solvents, failed to produce any definite crystalline form, but the melting point remained unchanged.

Found: C, 72·98%; H, 12·27%; Molecular weight 226.

$C_{13}H_{26}O_2$ requires: C, 72·9%; H, 12·15%; Molecular weight 214.

Fractions AII, AIII and AIV were eluted separately with acetone, the solvent removed by distillation and the residues separately dissolved in 1,2-dichloroethylene. These solutions were rechromatographed on activated alumina, the same solvent being used for developing the chromatograms. The following were the results:

Fraction AII. An upper weak orange band AII(i) and a lower yellow band AII(ii) developed. AII(i) was eluted with acetone and evaporated to dryness. A small orange-coloured residue resulted, which could not be further purified.

AII(ii) was eluted with acetone and worked up with AIII(iii).

Fraction AIII. On a tube of activated alumina this fraction developed three bands, AIII(i), AIII(ii) and AIII(iii).

The upper bands AIII(i) and AIII(ii) were eluted with acetone and the solutions evaporated. The resulting residues were however so minute that nothing could be isolated from them.

The lower band AIII(iii) washed through the tube very readily with the developing solvent, to form a light yellow solution with slight green fluorescence. The residue obtained on distillation of the solvent, together with that from AII(ii), was recrystallised from 20% dichloroethane in ethyl alcohol. This gave substance (ii) as yellow needles, m.p. 211°C. Substance (ii) was proved, by mixed melting points with authentic specimens, to be identical with the substance $C_{18}H_{16}O_6$, previously isolated from *Neorautanenia edulis*[4].

Fraction AIV. This fraction on activated alumina developed one broad yellow band, which was washed through the tube with 1·2-dichloroethylene and collected in three arbitrary fractions. On evaporation and crystallisation from 20% dichloroethane in ethyl alcohol, all three fractions gave the same product viz. substance (ii), m.p. 211°C. The combined mother liquors from these recrystallisations however, on slow evaporation, gave two different crystalline deposits. The first crop on recrystallisation from ethyl alcohol yielded substance (iii) as light-yellow prisms, m.p. 180°C. This was proved, by mixed melting points with an authentic specimen, to be identical with the compound $C_{19}H_{14}O_6$, previously isolated from Neorautanenia edulis[4].

The second crystalline deposit was recrystallised repeatedly from mixtures of chloroform and ethyl alcohol and gave substance (iv) as pale yellow, rod-like needles, m.p. 197°C.

Found: C,67·74%; H, 3·97%; Molecular weight 282.

$C_{15}H_{12}O_5$ requires: C, 67·61%; H, 4·22%; Molecular weight 284.

Fraction B. 3 g. of fraction B were dissolved in acetone, poured on a column of activated alumina and eluted with acetone. The solvent was removed by distillation

and the residue, dissolved in 15ml. 1·2-dichloroethylene, poured onto a column of activated alumina (66×1·5 cm.). The following bands appeared on developing with the same solvent:

Band	*Colour*	*Section of Column*
BI	Brown	Top
BII	Dark yellow	
BIII	Pale yellow	Bottom

The bands BII and BIII were readily washed through the column and collected separately, whilst BI had to be eluted with ethyl alcohol.

Fraction BI. The resinous residue, obtained by evaporation of the solvent, contained some crystals. After washing repeatedly with small amounts of ether, the crystals were purified by recrystallisation from aqueous acetone to yield substance (vi) in colourless, shiny flakes, m.p. 160°C.

Found: C, 82·21%; H, 11·63%; Molecular weight 270.

$C_{18}H_{30}O$ requires: C, 82·44%; H, 11·44%; Molecular weight 262.

Fraction BII. The residue on purification was found to be substance (ii).

Fraction BIII. On evaporating the solvent, a crop of colourless prisms was obtained, contaminated with some oil, which was removed by washing with ether. The material was purified by recrystallisation from n-butyl alcohol, which gave substance (v) as colourless, short prisms, m.p. 181·5°C.

Found: C, 67·61%; H, 3·72%; Molecular weight 379.

$C_{22}H_{14}O_7$ requires: C, 67·68; H, 3·59; Molecular weight 390.

Alkali Treatment of Fraction B

30 g. were dissolved in 250 ml. methyl alcohol on the waterbath and the brown solution cooled and filtered. This filtrate was rendered alkaline by careful addition of some strong sodium hydroxide solution, whereby a dark red colour developed in the solution and a precipitate (Fraction CI) was formed. The solution was filtered after a few days and water added to the filtrate, which precipitated a brown resin (Fraction CII). After coagulation of the resin, the brown supernatant liquid was poured off, and the methyl alcohol evaporated on the waterbath. The residual solution was acidified with acetic acid and extracted with ether (Fraction CIII). The acid solution was then made ammoniacal and again extracted with ether (Fraction CIV).

Fraction CI. The material dissolved in acetone was run through a column of activated alumina and, after removal of the acetone, the purified material was dissolved in dichloroethane and chromatographed on alumina. On development with the same solvent the following bands appeared in the tube:

Bands	*Colour*	*Section of Tube*
CI(i)	Red	Top
CI(ii)	Light yellow	
CI(iii)	Light orange	Bottom

The three bands were eluted from the column and three separate fractions obtained.

Fraction CI(i) was eluted with a mixture of acetone and ethyl alcohol and gave a crystalline residue on evaporation. Crystallisation from aqueous acetone produced substance (vi). Fraction CI(ii) yielded a negligible amount of material. Fraction CI(iii), eluted with dichloroethane, gave on evaporation of the solvent a crystalline material mixed with oily matter. The oil was removed with ether and the crystalline residue dissolved in n-butyl alcohol. Colourless crystals of substance (v) separated on cooling.

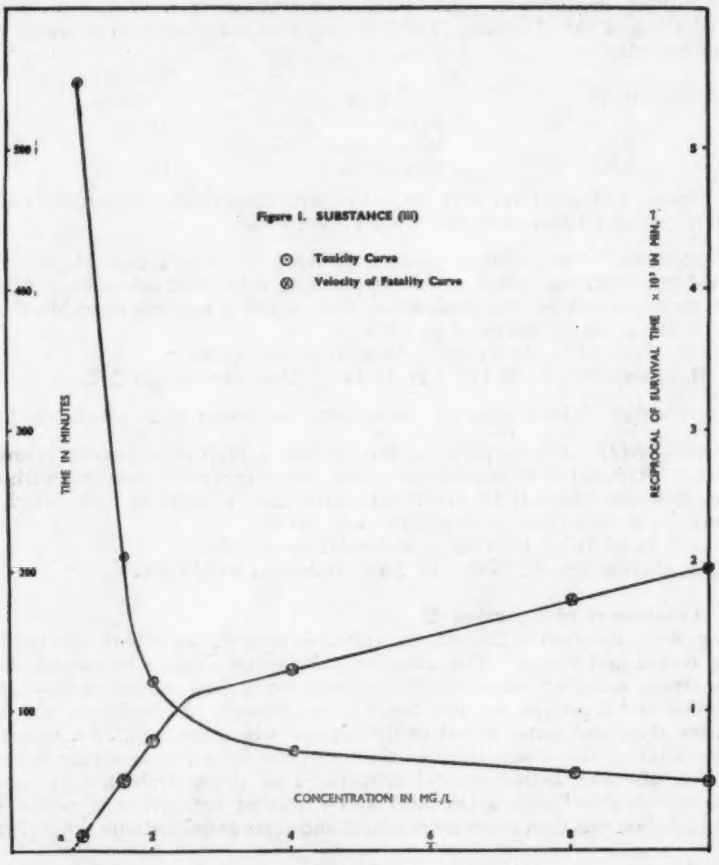

TABLE I

Toxicity to Lebistes reticulatus of substance (iii) at 25°C.

Concentration Milligrams per Litre	*Survival Time Minutes*	*Mean Survival Time in Minutes*	100 / *Mean Survival Time*
10	44 53	48·5	2·06
8	52 62	57	1·75
4	69 87	78	1·28
2	108 138	123·5	0·8 1
1·6	169 267	218	0·46
1	543 547	545	0·18

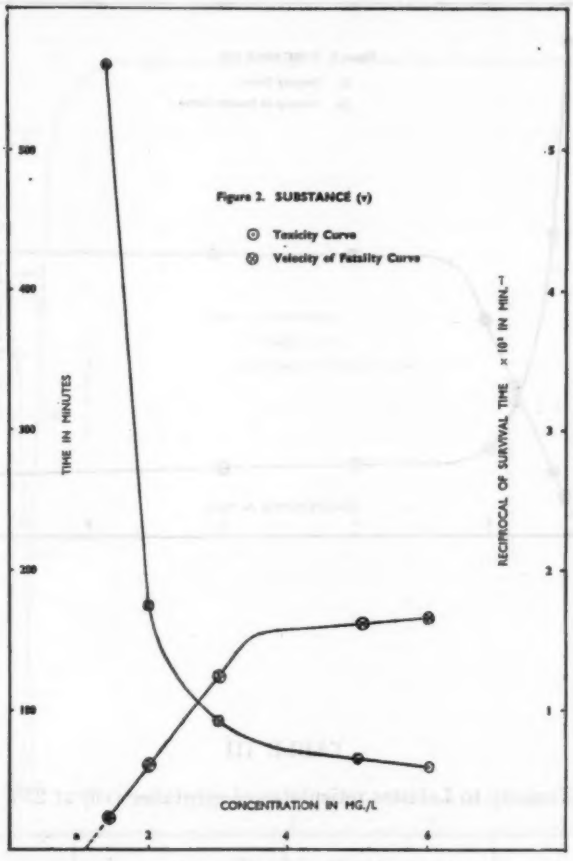

TABLE II

Toxicity to Lebistes reticulatus of substance (v) at 25°C.

Concentration Milligrams per Litre	*Survival Time Minutes*	*Mean Survival Time in Minutes*	100 / *Mean Survival Time*
6	59 61	60	1·67
5	69 52	60·5	1·65
3	74 94	84	1·19
2	166 179	173	0·58
1·4	529 519	524	0·19

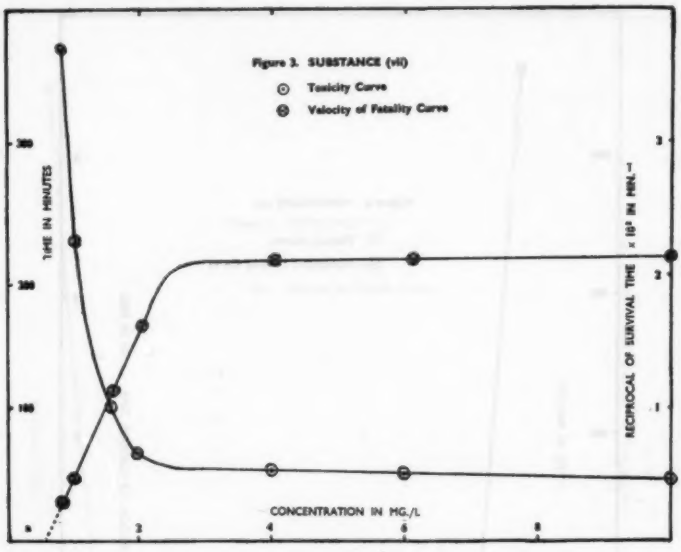

TABLE III

Toxicity to Lebistes reticulatus of substance (vii) at 25°C.

Concentration Milligrams per Litre	*Survival Time Minutes*	*Mean Survival Time in Minutes*	100 / *Mean Survival Time*
10	45 50	47·5	2·1
6	49 45	47·0	2·1
4	37 57	47·0	2·1
2	62 63	62·5	1·6
1·6	72 116	94	1·06
1·0	208 245	226·5	0·44
0·8	360 382	371	0·27

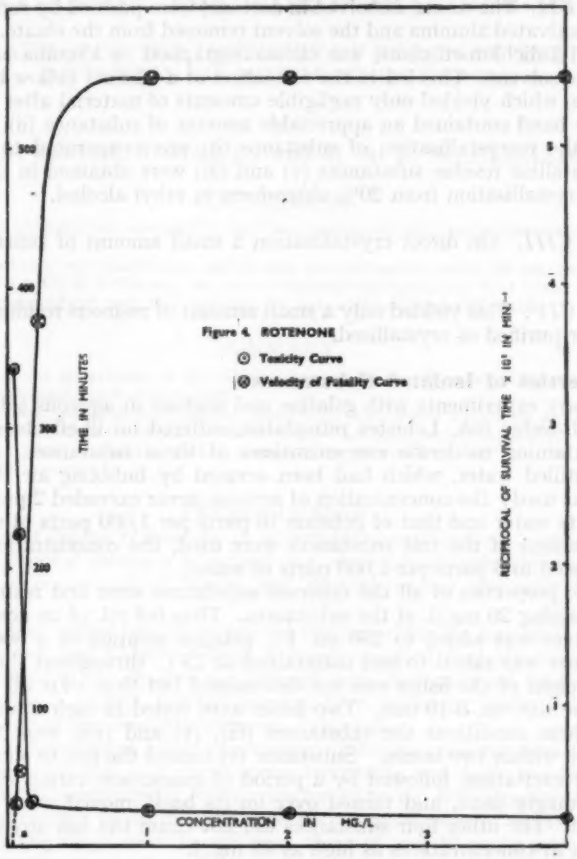

TABLE IV

Concentration Milligrams per Litre	*Survival Time Minutes*	*Mean Survival Time in Minutes*	100 / *Mean Survival Time*
4	20	18·6	5·4
	20		
	16		
	20	19	5·3
2	20		
	18		
	17	19	5·3
1·0	20		
	21		
	20	26·6	3·8
0·2	20		
	40		
0·1	220	213	0·47
	210		
0·05	295	333	0·3
	370		

Fraction CII. The resins, dissolved in acetone, were purified by running through a column of activated alumina and the solvent removed from the eluate. The residue, dissolved in 1,2-dichloroethylene, was chromatographed on alumina and developed with the same solvent. This led to the formation of a distinct yellow band and two weaker bands, which yielded only negligible amounts of material after elution. The bright yellow band contained an appreciable amount of substance (ii). The mother liquor from the recrystallisation of substance (ii) was evaporated to dryness and from the crystalline residue substances (v) and (iii) were obtained in that order, by fractional recrystallisation from 20% chloroform in ethyl alcohol.

Fraction CIII. On direct crystallisation a small amount of substance (ii) was obtained.

Fraction CIV. This yielded only a small amount of resinous residue which could not be further purified or crystallised.

Toxic Properties of Isolated Substances

Preliminary experiments with gelatine and acetone in aqueous solution showed that the fresh-water fish, Lebistes reticulatus, suffered no ill-effects when kept in solutions containing moderate concentrations of these substances. In all tests, therefore, distilled water, which had been aerated by bubbling air through it for five hours, was used; the concentration of acetone never exceeded 2 parts of acetone per 1,000 parts water and that of gelatine 10 parts per 1,000 parts of water. When low concentrations of the test substances were used, the concentration of gelatine could be reduced to 5 parts per 1,000 parts of water.

The toxic properties of all the different substances were first tested by using a solution containing 20 mg./l. of the substances. Thus 0·5 ml. of an acetone solution of the substance was added to 250 ml. 1% gelatine solution in a 600 ml. beaker, the temperature was raised to and maintained at 25°C. throughout the experiment. The actual weight of the fishes was not determined but they were all of approximately the same size viz. 8-10 mm. Two fishes were tested in each solution.

Under these conditions the substances (iii), (v) and (vii) were toxic to fish, being effective within two hours. Substance (v) caused the fish to show immediate signs of great excitation, followed by a period of quiescence during which the fish, although seemingly dead, and turned over on its back, moved away very rapidly when touched. The other four substances did not cause the fish any apparent discomfort, even at concentrations as high as 40 mg./l.

From tests carried out under these conditions, the toxicity and velocity of fatality curves of substances (iii), (v) and (vii) were constructed (Figures 1, 2 and 3). The same was done for rotenone (Figure 4) under similar conditions, except that, in the case of rotenone, the protective colloid was not used. The results of the different tests are given in the tables.

The authors thank the University of South Africa for a Post-Graduate Exhibition awarded to one of them (N.S.).

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PROPERTIES OF THE BORON HALIDES PART IV

THE SEPARATION OF THE ISOTOPES OF BORON BY THE THERMAL DIFFUSION OF BORON TRIFLUORIDE

by

B. A. COOKE, J. HAWES and H. A. E. MACKENZIE*

OPSOMMING

'n Kolom is ontwerp en vervaardig om boor-isotope te skei deur hittediffusie van boortrifluoried.

Die tien voet roesvrye staalkolom, gevul met boortrifluoried onder 55 sm. druk in 'n ringopening met strale 0·635 en 1·120 sm., het 'n ewewigskeidingsfaktor van 1·14 binne agt uur gegee, met 'n temperatuurgradient van 780° per sm., en kragverbruik van 980 watt.

SUMMARY

A column for the separation of the boron isotopes by the thermal diffusion of boron trifluoride has been designed and constructed.

The ten foot long, stainless steel column, when filled with boron trifluoride at 55 cm. pressure in an annular space of radii 0·635 and 1·120 cm., gave an equilibrium separation factor of 1·14 in less than eight hours operation with a temperature gradient of 780° per cm. and a power consumption of 980 watts.

INTRODUCTION

The choice of boron trifluoride as a suitable compound of boron for isotope separation by physical means is a natural one, since boron trifluoride is the lightest thermally stable compound of boron, and fluorine occurs naturally in only one isotopic form.

An attempt at separation by means of thermal diffusion has been reported by Watson, Buchanan and Elder[1]. These workers assumed that the viscosity of the gas and the temperature dependence thereof were the same as those of sulphur dioxide. That this is, in fact, not the case has been shown by Cooke and Mackenzie in a recent study[2] of the viscosity of boron trifluoride.

Watson, Buchanan and Elder experienced difficulties arising from the presence of impurities (notably SiF_4) in their boron trifluoride and from the low resolving power of their mass spectrometer; they were forced to use B^{3+} ions for their isotopic analysis, with prejudice to accuracy[3], since they were unable to resolve the 48 and 49 peaks due to the BF_2^+ ions. In addition, their 48 and 49 peaks were overlapped by other, presumably residual, peaks.

It seemed desirable, in the light of the newly available viscosity data and the experience of Watson, Buchanan and Elder, to re-examine the problem of separating the boron isotopes by the thermal diffusion of the trifluoride. The results have justified this and reveal the feasibility of a continuous separation process employing columns in cascade.

COLUMN DESIGN

The most accessible starting point in the design of a thermal diffusion column is a knowledge of the viscosity and its temperature dependence for the gas under investigation[4, 5]. Jones and Furry[5], in particular, have reviewed extensively those theoretical considerations which provide a basis for design, and we shall not elaborate on these here. Our calculations are based on their theoretical treatment and we shall employ their notation and symbols. Reference to equations or tables which appear in their review will be made, where necessary, by the letters J.F. followed by the number of the relevant equation or table, e.g. J.F. (100).

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The column planned by us was to be of the coaxial tube type to operate between 400°C and room temperature with a mean temperature of about 483°K. The approach to the problem of design was first to estimate a width for the annular gas space which would give satisfactory operation at atmospheric pressure, then to select tubing satisfying the calculated requirement as well as possible and finally to calculate the transport coefficients in terms of gas pressure and decide upon an operating pressure which should give a moderate enrichment without an unduly slow approach to equilibrium.

The calculations are summarised below.

Viscosity. A short extrapolation of the data obtained by Cooke and Mackenzie (*loc. cit.*) gives

$$\eta = 2{\cdot}524 \times 10^{-4} \text{ g.cm.}^{-1} \text{ sec.}^{-1} \text{ at } 483°\text{K}.$$

Repulsive force index for the inverse power model. The curve obtained by plotting $\log\eta$ against log T has a slope which decreases with increasing temperature; the rate of decrease itself falls off, however, and the slope is substantially constant at 0·788 in the range 410 to 470°K. It is reasonable to assume, then, that

$n = 0{\cdot}788$ at 483°K, and hence, J.F.(13):

$\nu = 7{\cdot}94$.

Thermal diffusion constant. J.F.(10):

$\alpha = 2{\cdot}36 \times 10^{-3}$.

Thermal conductivity. By a long extrapolation of the constant pressure molar heat capacity data due to Millar[6] and the application of the equation $C_p - C_v = \mathbf{R}$ we have estimated that $c_v = 0{\cdot}20$ cal. g.$^{-1}$ deg.$^{-1}$ at 483°K and hence[7],

$$\lambda = 1{\cdot}3 \times 10^{-4} \text{ cal. cm.}^{-1} \text{ sec.}^{-1} \text{ deg.}^{-1}$$

Coefficient of ordinary diffusion. With the pressure, p, in atmospheres,

$$\rho = 1{\cdot}71 \times 10^{-3} p \text{ g. cm.}^{-3} \text{ at } 483°\text{K}.$$

J.F. (Table I): $\frac{6}{5}f(7{\cdot}94) = 1{\cdot}46$, and hence, J.F.(18):

$$D = \frac{0{\cdot}215}{p} \text{ cm.}^2 \text{ sec.}^{-1}$$

Transport Coefficients. By assuming a reasonable value for the ratio B/2w, say 15·0, one can express the transport coefficients in terms of p and 2w only. One obtains,

J.F.(70): $H^{(o)} = 3{\cdot}46 \times 10^{-4} p^2 (2w)^4$ g. sec.$^{-1}$

J.F.(71): $K_c^{(o)} = 0{\cdot}901\ p^4 (2w)^8$ g. cm. sec.$^{-1}$

J.F.(72): $K_d^{(o)} = 5{\cdot}52 \times 10^{-3} (2w)^2$ g. cm. sec.$^{-1}$

These transport coefficients apply to the case of thermal diffusion between two plane parallel vertical walls without end effects, so that cylindricity has not yet been taken into account.

Estimation of a suitable width for the annular space. The equilibrium separation factor is given by

J.F.(150): $q_e = e^{2AL}$,

where $A = H/2K$ and $K = K_c + K_d + K_p$. If we neglect K_p, q_e will have a maximum value when 2w is so chosen that $K_c/K_d = \frac{1}{2}$. This condition is difficult of attainment, since K_c/K_d is proportional to $(2w)^6$, (neglecting cylindricity corrections which depend less strongly on 2w.) Fortunately K_c/K_d can be made as large as 25 without the equilibrium separation factor being very greatly decreased, although this particular ratio constitutes a theoretical limit, set by Reynolds' criterion, above which turbulence may set in. Experimentally[8], higher values have been employed without turbulence becoming detectable. When the efficiency of a column is considered in relation to power consumption, however, it would seem that the optimum condition[9] is that $K_c/K_d = 10$.

With this choice for the ratio and a pressure of 0·90 atm. (slightly less than the prevailing atmospheric pressure in Pietermaritzburg), one obtains

$2w = 0{\cdot}459$ cm.

Stainless steel tubing could be obtained in such dimensions as to give $2w = 0{\cdot}485$ cm. and $B/2w = 11{\cdot}4$, and this was considered to be satisfactory. The inner tube had an external diameter of 1·270 cm. and the outher tube had an internal diameter of 2·240 cm. The power consumption and optimum gas pressure were then calculated using these values.

Power consumption. The heat loss by radiation was calculated by Stefan's law, using as the emissivity of the 18/8 stainless steel employed a value[10] of 0·4, and found to be 400 watts for the 287 cm. heated. The loss by conduction was estimated from the thermal conductivity calculated above and found to be 640 watts, giving a total power consumption of 1040 watts.

As will be seen when the column is described, the temperature at the inside of the hot tube was the one measured and it is easily shewn from the thermal conductivity of stainless steel[10] that the temperature drop across the inside hot tube, which had an inner radius of 0·44 cm., was about 0·8°C for a power consumption of 1 kilowatt. 1·25 litres of water per minute flowed through the cooling jacket and, at this rate, the rise in temperature of the water was about 10°C. The figures $\Delta T = 380°$ and $T = 483°K$ were therefore retained in the rest of the calculation.

Pressure for maximum separation (p_m). The transport coefficients were recalculated from the actual apparatus dimensions and with the application of the appropriate cylindricity corrections.

J.F.(70,109,110,111): $H = 1{\cdot}67\times10^{-5}p^2$ g. sec.$^{-1}$

J.F.(71,101,105,106): $K_c = 2{\cdot}91\times10^{-2}p^4$ g. cm. sec.$^{-1}$

J.F.(72,102,107,108): $K_d = 9{\cdot}64\times10^{-4}$ g. cm. sec.$^{-1}$

If we set $K_p = r.K_c$, it is easily shewn from J.F.(150,70,71,72 and 18) and from the quantities calculated above that

$$\log q_e = \frac{5{\cdot}74\times10^{-4}\times287p^{-2}}{1+r+3{\cdot}31\times10^{-2}p^{-4}}$$

for a column of the dimensions chosen by us. It is not possible to calculate r but, even if it is as large as 1·0, the effect on the pressure for maximum separation factor is not large. Naturally, though, its effect on the equilibrium separation factor is considerable. In our case, setting $(d \log q_e/dp)_p = p_m = 0$, we obtain

$p_m = 0{\cdot}43$ atm for $r = 0$

and $p_m = 0{\cdot}36$ atm. for $r = 1$.

Agreement between calculated pressures for maximum separation and observed ones has not been especially good[11] and, in this study, the value obtained from viscosity data has been used only as a guide. Experimental results[11,12] have consistently shewn that the rate of approach to equilibrium is less when the column is run at p_m than it is for higher pressures and this fact has been borne in mind in the choice of operating conditions for our column.

DESCRIPTION OF THE COLUMN

The top end detail of the column is shewn in Fig. 1 and the bottom end detail and spacer arrangement in Fig. 2. The stainless steel inner hot tube, A, 10 ft. 0¾ in. long, was silver-soldered to a ⅛ in. stainless steel flange, F. A ⅛ in. diameter, 2 in. long steel tube, T, housing a chromel-alumel 0·005 in. wire thermocouple, was silver-soldered to the inner wall of A. The lower closed end of T lay 7 in. below the top end of A. A steel side-arm, C, machined to fit a B16 ground glass socket, was silver-soldered at the side of the outer stainless steel tube, B. Another ⅛ in. flange was silver-soldered to the top of B. Vacuum tightness was obtained by using a specially moulded polythene gasket, P, between the flanges.

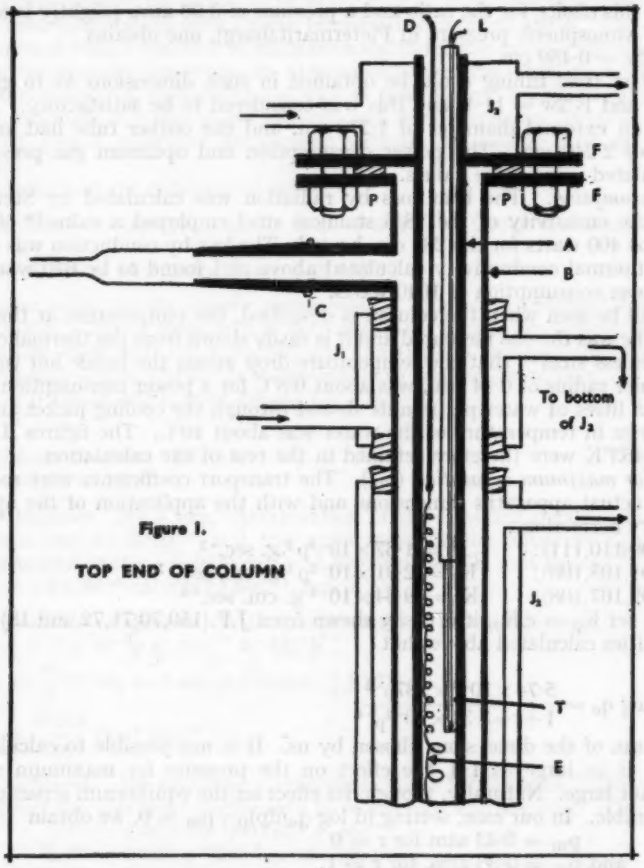


Figure 1.

TOP END OF COLUMN

The heating element, E, of 22 gauge nichrome wire, was a helical coil of internal diameter $\frac{1}{8}$ in. The top part of the coil was made narrower, to fit past T, but more closely spaced to compensate for this. The disposition of the coils along the length of the tube was carefully arranged so that, on heating up the polished tube in air, superficial oxidation occurred at a uniform rate over its whole length. Sagging of the heater coils was prevented frictionally by the cylindrical asbestos paper insulators along its length. This was carefully checked over long periods. Connection to E was made by a lead of stout copper wire, D. At the bottom, E was twist-joined to a thin wire nail which was silver soldered through a plug, Q, at the bottom of the hot tube. The metal parts of the column were connected to the earthed side of the 220 volt mains and D, through a rheostat and ammeter, to the live side of the mains.

The spacers between A and B were of unusual design. No metal protruded from the hot tube which might create parasitic convection currents. The spacers were made from lengths of clock spring, R (Fig. 2), 6·9 cm. long, small ceramic bead insulators, S, and short lengths of copper wire, M, drawn out to such a diameter as just to pass through the holes in the beads. The clock spring was first annealed so that holes for the insertion of the copper wire could be drilled and the temper sub-

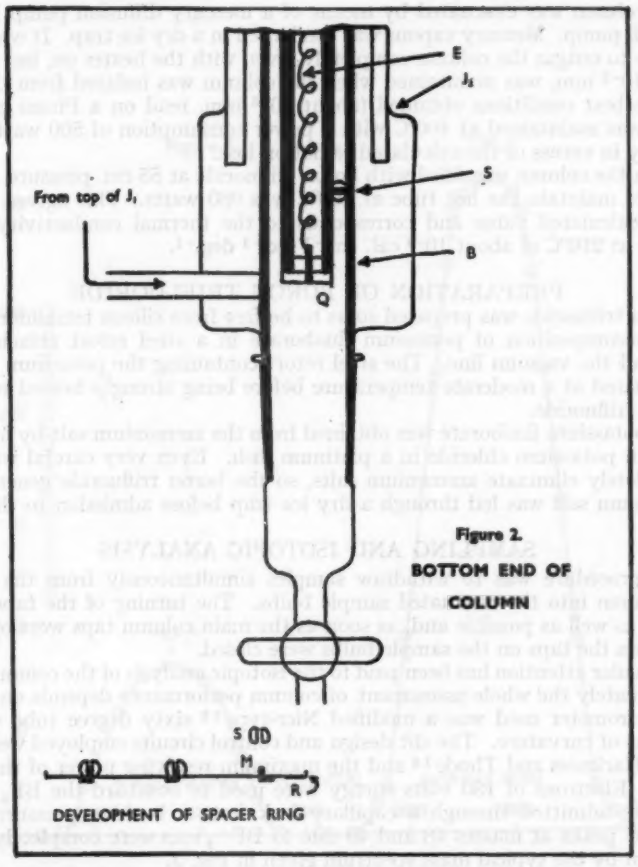


Figure 2.
BOTTOM END OF COLUMN

sequently restored by quenching the red hot strip in oil. Lengths of copper wire, M, riveted at one end, were soldered to the strips so as to protrude some 2 or 3 mm. The beads were ground on a carborundum wheel to fit each spacer individually so that the total width of a spacer was 4·81 mm. within a tolerance of 0·02 mm. This measurement was found to give certain spacing and yet allow working clearance for the assembly of the column and for the tube movement due to expansion while heating. Four spacers were used, one at the bottom and the others at intervals of 2 ft. 6 in. up the column.

Connection of the column to glass apparatus at the bottom was made with a stainless steel tapered cone on which fitted a B24 ground glass socket.

Three cooling jackets were fitted. Cold water from a constant head tank entered the short jacket J_1 and was led to the bottom of the main jacket J_2. The small jacket J_3 passed a trickle of water which cooled the flanges and prevented damage to the polythene gasket. The grease on C was kept cool by the water in J_1.

The glass sample lines were constructed so as to have as small a volume as possible. Sample bulbs of about 20 cc. capacity could be attached by means of ground glass joints.

The column was evacuated by means of a mercury diffusion pump backed by a rotary oil pump. Mercury vapour was condensed in a dry ice trap. It was virtually impossible to outgas the column completely, even with the heater on, but a pressure of about 10^{-3} mm. was maintained when the column was isolated from the pumps. Under the best conditions obtained (about 10^{-5} mm. read on a Pirani gauge), the hot tube was maintained at 400°C with a power consumption of 500 watts. This is not greatly in excess of the calculated radiation loss.

When the column was filled with boron trifluoride at 55 cm. pressure, the power required to maintain the hot tube at 400°C was 980 watts. This agrees fairly well with the calculated value and corresponds to the thermal conductivity of boron trifluoride at 210°C of about 10^{-4} cal. $cm.^{-1}$ $sec.^{-1}$ $deg.^{-1}$.

PREPARATION OF BORON TRIFLUORIDE

Boron trifluoride was prepared so as to be free from silicon tetrafluoride by the thermal decomposition of potassium fluoborate in a steel retort attached to the column and the vacuum line. The steel retort containing the potassium fluoborate was evacuated at a moderate temperature before being strongly heated to generate the boron trifluoride.

The potassium fluoborate was obtained from the ammonium salt by hot precipitation with potassium chloride in a platinum dish. Even very careful washing did not completely eliminate ammonium salts, so the boron trifluoride generated from the potassium salt was led through a dry ice trap before admission to the column.

SAMPLING AND ISOTOPIC ANALYSIS

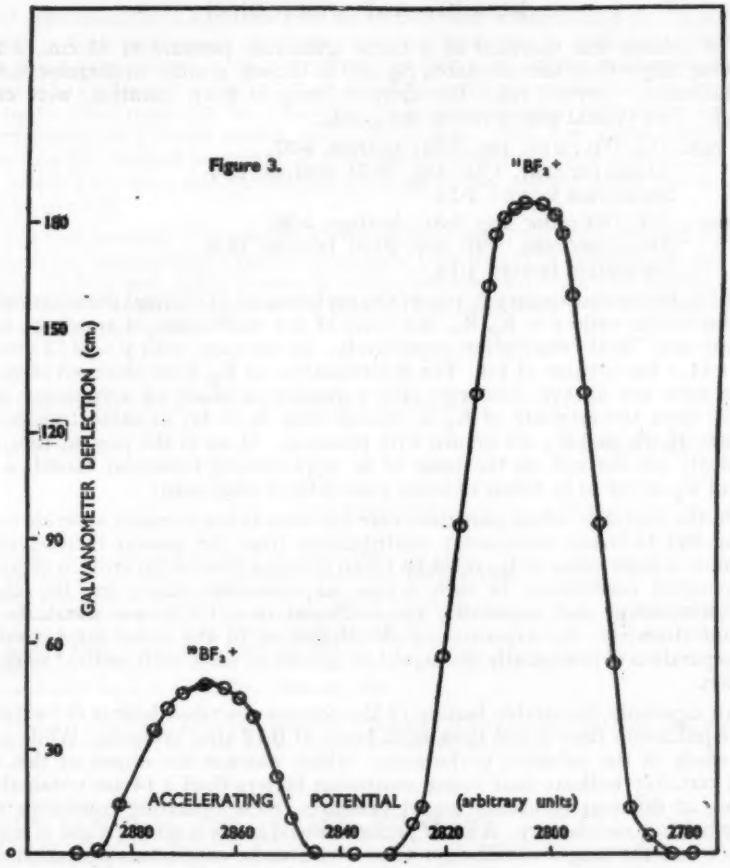
Our procedure was to withdraw samples simultaneously from the two ends of the column into the evacuated sample bulbs. The turning of the taps was synchronised as well as possible and, as soon as the main column taps were open to the sample lines the taps on the sample bulbs were closed.

Particular attention has been paid to the isotopic analysis of the column samples, since ultimately the whole assessment of column performance depends on this. The mass spectrometer used was a modified Nier-type[13] sixty degree tube with a six inch radius of curvature. The slit design and control circuits employed were those of Graham, Harkness and Thode[14] and the maximum resolving power of the slits was 1 in 130. Electrons of 130 volts energy were used to bombard the BF_3 molecules which were admitted through a capillary leak from a backing pressure of about 6 cm. The peaks at masses 48 and 49 due to BF^+_2 ions were completely resolved, as is shewn by the typical mass spectrum given in Fig. 3.

Inghram[15] reported marked deviations from linearity when scanning these peaks by varying the accelerating potential with constant magnetic field and had to apply corrections when using voltage scanning.

This difficulty was not experienced by us. The conditions of focus at the ion source of our instrument were sufficiently good for the mass spectrometer to behave quite linearly over the voltage range embracing the peaks at masses 48 and 49. This was ascertained by comparing the ion currents obtained respectively by voltage and magnetic scanning.

Prior to the admission of boron trifluoride, the mass region to be studied was shewn to be free from residual peaks. Between analyses the mass spectrometer tube and sample line on the high pressure side of the capillary leak were pumped out until the height of the $^{11}BF^+_2$ peak was reduced to 1·5 per cent of its former value. The error which would be incurred by not eliminating the peak completely can be shown to be quite negligible. The abundance ratios reported here were obtained by magnetic scanning, the accelerating potential being altered very slightly (never more than 0·5 volt) in order perfectly to locate the maximum of a peak. This procedure was necessitated by the coarseness of the magnet control compared with that of the accelerating potential.



Four successive determinations of the boron abundance ratio with natural boron trifluoride prepared from potassium fluoborate gave

$^{11}BF^+_2/^{10}BF^+_2 = 4{\cdot}26, 4{\cdot}24, 4{\cdot}22, 4{\cdot}24.$

Using the packing fractions of Bainbridge[16] of $16{\cdot}3\times10^{-4}$ and $11{\cdot}8\times10^{-4}$ for ^{10}B and ^{11}B respectively, and the factor 1·000275 to convert from the physical to the chemical scale, a value of 4·24 for the ratio $^{11}BF^+_2$ gives the atomic weight of boron as 10·820, in good agreement with the accepted value. Variation in the abundance ratio of 0·02 (viz., that obtained experimentally) corresponds to a variation of only 0·001 in the atomic weight.

The difference between our abundance ratio (4·24) and that obtained by Inghram (4·31) does not, in our opinion, reflect adversely on either determination, since slight variations in the $^{11}B/^{10}B$ ratio for natural boron are well established[17]. The precision of our determinations is clearly adequate for reliance to be placed on the analysis of samples from the thermal diffusion column.

RESULTS AND DISCUSSION

The column was operated at a boron trifluoride pressure of 55 cm., a figure somewhat larger than the calculated p_m and so chosen in order to decrease the time to equilibrium. Several runs, the shortest being of 8 hr. duration, were carried through. Two typical sets of results are given.:

48 *hr. run.* $^{11}B/^{10}B$ ratio: top, 3·83; bottom, 4·37.
Atoms per cent. ^{10}B: top, 20·7; bottom, 18·7.
Separation factor: 1·14.

8 *hr. run.* $^{11}B/^{10}B$ ratio: top, 3·81; bottom, 4·35.
Atoms per cent. ^{10}B: top, 20·8; bottom, 18·8.
Separation factor: 1·14.

It has become customary to report the performance of thermal diffusion columns in terms of the ratio $r = K_p/K_c$, the ratio of the coefficients of transport due to parasitic and "ideal" convection respectively. In our case, with $p = 0·72$ atm. and $q_e = 1·14$, r has a value of 1·3. The determination of K_p from observed separation factors does not always, however, give a reliable estimate of asymmetry in the column, since the estimate of K_p is reliable only in so far as other transport coefficients, H, K_c and K_d are known with precision. If, as in the present case, these coefficients are derived on the basis of an approximate molecular model, a large value of K_p is not to be taken to mean poor column alignment.

On the contrary, where particular care has been taken to ensure accurate column spacing and to reduce asymmetry contributions from the spacers themselves to a minimum, a large value of K_p must be taken to mean theoretical error in estimating the transport coefficients. In such a case, experimental values for the thermal diffusion constant and, especially, the coefficient of self diffusion should be used but, unfortunately, the experimental determination of the latter must await the prior separation of isotopically distinguished species by some such method as thermal diffusion.

An especially favourable feature of the column described here is the extremely short equilibrium time of less than eight hours at 0·72 atm. pressure. While a complete study of the column's performance, which was not the object of this work, would certainly indicate that larger separation factors than 1·14 are obtainable by working at different (probably lower) pressures, these operating conditions would hardly be more satisfactory. A lower pressure would imply a smaller yield of enriched product and the longer equilibrium time would make continuous operation of the column not a feasible proposition. One of the objects of this work was to provide a basis for planning continuous production of boron trifluoride enriched in ^{10}B.

From our results it is evidently possible to produce at least 45 cc. of boron trifluoride, whose boron content contains 20·8 atoms per cent. ^{10}B, per eight hours operation, since the volume of the upper sampling line and bulb was 45 cc.

In this connection it is interesting to note the recent work of Green and Martin[18] who distilled boron trichloride through a packed column and achieved a separation of the boron isotopes. Thermal diffusion with our apparatus gives a separation factor equivalent to that which would be achieved by a 73-plate distillation of boron trichloride. Unfortunately the two methods cannot be compared here from the point of view of quantity production of ^{10}B, since Green and Martin do not state in their paper the time to equilibrium for their distillation column.

A direct comparison of our results with those of Watson, Buchanan and Elder (*loc. cit.*) is difficult, because their apparatus was in three separate convectively-coupled units of 3 m., 3 m., and 1 m. lengths. Over the first two units (6 m. length) they found a separation factor of 1·2, which compares unfavourably with our result. On the other hand, they claim a separation factor of 1·1 for the last 1 m. unit. This

would correspond to a separation factor of 1·77 over a length of 6 m. It is difficult to explain this discrepancy on the presence of impurities in their boron trifluoride, since these rarely amount to more than one per cent. in the modern commercial product[19]. Further, it is difficult to reconcile with the values obtained by Inghram[15] and by us, their result for the ratio $^{11}B/^{10}B$ in natural boron trifluoride, viz., 3·88, corresponding to a boron atomic weight of 10·806. Their low value cannot be explained on the basis of impurities in their boron trifluoride, since none of the impurities which have been encountered in the commercial product gives rise to a mass peak at 10 or 11.

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PROPERTIES OF THE BORON HALIDES PART V

THE INTERMOLECULAR FORCE CONSTANTS OF BORON TRIFLUORIDE

by

C. J. G. RAW

OPSOMMING

Die intermolekulêre kragkonstantes van boortrifluoried is uit onlangse eksperimentele viskositeitsgegewens bereken. Die waardes is $\epsilon/k = 170°K$ en $r_o = 4{\cdot}266$ Å. Hierdie konstantes word in verband met sekere ander eienskappe van boortrifluoried bespreek.

SUMMARY

The intermolecular force constants of boron trifluoride have been calculated from recent experimental viscosity data. The values are $\epsilon/k = 170°K$ and $r_o = 4{\cdot}266$ Å. These constants have been discussed in connection with certain other properties of boron trifluoride.

The boron trifluoride molecule is symmetrical and non-polar[1] and it should therefore be possible to describe the molecular interactions in this gas by a potential energy function of the Lennard-Jones type.[2]:

$$E(r) = 4\epsilon\,[(r_o/r)^{12} - (r_o/r)^6]$$

where E(r) is the potential energy of the two molecules when the separation between their centres is r, ϵ is the maximum energy of attraction, and r_o is the collision diameter for low-energy head-on collisions.

The transport coefficients of simple non-polar gases, being strongly dependent on the intermolecular forces, provide a very satisfactory means[3] of determining the force constants ϵ and r_o.

Recent experimental data on both the viscosity[4] and the thermal conductivity[5] of boron trifluoride are available. However, the theory in the case of the thermal conductivity, depending as it does on the Eucken assumption that during molecular collisions thermal equilibrium is established between the translational and internal degrees of freedom of the molecules, is probably not valid for boron trifluoride. In addition, the molar heat capacity at constant volume, at present unknown for boron trifluoride, is involved in the theoretical expression for the thermal conductivity.

For these reasons, the viscosity was used to predict the force constants by the method of Hirschfelder, Bird, and Spotz[2]. The theoretical expression for the viscosity at various temperatures involves complicated functions of the "collision integrals" which have been computed and tabulated by these authors for various values of kT/ϵ (k = Boltzmann's constant, T = temperature in degrees Absolute). By trial and error, values of ϵ/k and r_o are chosen which on substitution in this equation give values of the viscosity at various temperatures which agree exactly with the experimental results. This method gives $\epsilon/k = 170°K$ and $r_o = 4{\cdot}266$ Å. The following table shows a comparison between the experimental and calculated values of the viscosity (η) in $g.cm.^{-1}sec.^{-1}$ at various temperatures.

T (°K)	kT/ϵ	$10^7\eta$(calcd.)	$10^7\eta$(exp.)
306	1·8	1732	1730
340	2·0	1899	1898
391	2·3	2134	2135
425	2·5	2284	2288
459	2·7	2438	2429

A rough indication of the value of ϵ/k can be obtained from the boiling point, T_b, and the critical temperature, T_c. Use is made of two approximate relations from the Lennard-Jones and Devonshire theory of gases and liquids[6]:

$$\epsilon/k \sim 0{\cdot}75T_c$$
$$\epsilon/k \sim 1{\cdot}39T_b$$

For boron trifluoride, from the critical temperature, $\epsilon/k = 196°K$, and from the boiling point, $\epsilon/k = 239°K$, both of which are rather high compared with the accurate value deduced above. The same theory gives the following approximate relation between r_o and V_c, the critical volume:

$$r_o \sim (8{\cdot}33 \times 10^7)\ (V_c)^{1/3}$$

from which $V_c \sim 1{\cdot}193\ cm^3.g^{-1}$.

From spectroscopic data[1], the diameter of the BF_3 molecule is 4·14 A, and this is in fairly good agreement with the value of 4·266Å for the collision diameter.

The most recent value of the compressibility coefficient of boron trifluoride at 0°C is 0·0060[1]. The second virial coefficient calculated from this is—133·8 $cm^3.mole^{-1}$. From the values of ϵ/k and r_o, the second virial coefficient is calculated by the Lennard-Jones theory[7] to be—102·1 $cm^3.mole^{-1}$.

The agreement between theory and experiment is satisfactory as far as available knowledge of the properties of boron trifluoride is concerned. Further evidence should be obtained from an investigation of thermal diffusion or diffusion in this gas, or from accurate determination of the second virial coefficient over a wide range of temperatures.

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SOME CONSTITUENTS OF THE RESIN OF *EURYOPS FLORIBUNDUS* N.E.BR.

by

D. H. S. HORN, J. R. NUNN and D. E. A. RIVETT

OPSOMMING

Die hars van *Euryops floribundus* bevat vry sure, esters en spore van langketting versadigde koolwaterstowwe. Meeste van die sure is geïdentifiseer, terwyl verskeie verbindings uit die onverseepbare material afgeskei is.

SUMMARY

The resin of *Euryops floribundus* has been found to contain free acids, esters and traces of saturated long chain hydrocarbons. The bulk of the free and combined acids has been identified, while several constituents of the unsaponifiable material have been isolated in a state of purity and partly characterised.

Euryops floribundus, a robust bush 5-10 feet high, which occurs extensively in the Eastern Cape Province, is one of about fifty species found in South Africa. As it is resistant to arid conditions it propagates readily, and has spread extensively on overgrazed and denuded veld. Its eradication has now become a serious problem to farmers in many areas. It has a resinous bark and is known locally as "Harpuisbos" (Resin bush). The properties of the resin of this species have been recorded by van der Merwe[1].

A microscopic examination of stem sections showed that the resin occurs partly in the cells of the bark and partly as an exudate on the surface. As it was not possible to remove easily the bark from the wood, the dried stems, freed from leaves, were extracted with cold acetone. The resin so obtained, in a yield of 7·7%, was subdivided by conventional means into free acids, combined acids, and unsaponifiable matter.

The combined acids were found to consist mainly of anisic, *iso*-butyric, angelic and tiglic acids. The free acids were a mixture of the same acids as those above, except that tiglic acid was absent. It is possible that the tiglic acid may have arisen by isomerization of part of the angelic acid. In addition, the free-acid fraction contained a large quantity of resinous acids.

The unsaponifiable material—a resinous oil—proved to be a very complex mixture, and has only been partly resolved into pure compounds. The only one isolated in any quantity (*ca.* 10%) was a substance with a melting point of 230-232°, for which the name *Euryopsonol* is proposed. It was shown on analysis to have the empirical formula $C_{15}H_{20}O_3$. On hydrogenation, hydrogen equivalent to two double bonds was taken up. It formed a mono-acetate, m.p. 196-198°, and a mono-2:4-dinitrophenylhydrazone, m.p. 288·5-289°. Chromic acid oxidation showed the presence of one C-methyl group. A Zeisel determination for O-alkyl was negative. An infra-red examination of euryopsonol in chloroform solution confirmed the presence of a hydroxyl linkage (probably primary) and a double bond. It also showed the presence of a ketonic linkage, but the absence of ether, anhydride, aldehyde or acid linkages. The possibility of an epoxide grouping cannot be ruled out, but the evidence of its presence is not definite. The ultra-violet spectrum, obtained in ethanol, had a broad band with a maximum at 279mμ (log E 4·18). Unfortunately we have not been able to continue the study of this compound because it has not been possible to isolate it from plant material collected recently.

Chromatography of the unsaponifiable material, followed in some cases by vacuum distillation in an efficient spinning-band fractionating column, yielded several other compounds. These were obtained in very small amounts, and in most cases insufficient material was available for a thorough study. From a mixture of

hydrocarbons, obtained by chromatography, one fully saturated hydrocarbon, m.p. 66·0-66·2°, was isolated. It was shown on analysis to have the formula $C_{33}H_{66}$. The X-ray long crystal spacing (39·8A) places the length of the carbon chain at about C_{30}.

The fraction which was slightly more strongly absorbed on alumina than the hydrocarbons yielded two further compounds on distillation: the one, m.p. 105·5-106·5°, has been tentatively assigned the formula $C_{18}H_{26}O_3$, and the other, m.p. 163·5-165°, the formula $C_{17}H_{24}O_3$. Both compounds were found to contain one methoxyl group. Distillation of the fractions even more strongly adsorbed on alumina yielded an alcohol $C_{23}H_{48}O$, m.p. 74-74·5° (acetate, m.p. 55-55·5°), which is thought to be *n*-tricosanol (literature m.p. 73·5-74·5°).

EXPERIMENTAL

M.p.s. are corrected

Extraction of the Resin

The plant material was obtained through the kind services of the Division of Botany and Plant Pathology, Pretoria, and was collected in the Graaf-Reinet district during June 1949. It was air dried, and the leaves removed by vigorous shaking. The branches were cut into small pieces for extraction without removal of the bark which was very firmly attached to the wood. Extraction with various solvents in a soxhlet gave the following yields of resin: acetone, 9·2%; heptane, 6·4%; ether, 12·3%; ethanol, 13·8%. These extractions were done on small branches, in which the ratio of bark to wood was higher than for the larger branches, and hence the yield of resin was higher than when the whole bush was extracted.

The material (8·64 kg.) was steeped in acetone for 24 hours. This process was repeated twice more, the third extraction yielding only a trace of resin. Evaporation of the combined extracts, finally in a vacuum, yielded a dark coloured semi-solid resin (660 g.; 7·7%).

Fractionation fo the Resin

The resin (479 g.) in ether (3 l.) was washed with water. Evaporation of the water (2 l.) yielded a sticky gum (3·5% of resin) which was discarded. The ethereal solution was then shaken with 5% sodium hydroxide solution until a colourless extract of the latter was obtained (3 l. used)-Fraction II. The ethereal solution was washed with water, dried (Na_2SO_4) and the ether evaporated, leaving a dark semi-solid residue (260 g.; 54·5% of the total resin)-Fraction I.

Fraction I contained considerable amounts of esters (Found: saponification value, 150; unsaponifiable matter, 63·0%; iodine value, 99·5). The material (260 g.) was dissolved in ethanol (500 c.c.) containing potassium hydroxide (65 g.) and refluxed for 6 hours. The mixture was diluted with water and extracted with ether. Evaporation of the ether from the dried solution (Na_2SO_4) left a semi-solid residue (133 g.; 27·8% of the total resin)—Fraction III.

The Combined Acids

The aqueous solution was acidified with hydrochloric acid and extracted continuously with ether for several hours. Owing to the large amount of ethanol present in the aqueous extract, the extracted acids had become partly esterified during the extraction. Hence, after the ether had been removed from the extract, potassium hydroxide (40 g.) was added. After standing for two days, the solution was refluxed for 1 hour during which time it turned black. Water was added, the alcohol distilled off, and the acidified solution continuously extracted with ether. Evaporation of the dried (Na_2SO_4) ethereal extract left a black liquid, which was distilled until the temperature had reached 240°/650 mm. The above distillate (51·5 g.) was redistilled at 656mm. pressure in a fractionating column which has an efficiency equivalent to approximately 22 theoretical plates. The results are given in Table I.

TABLE I

Fraction	Weight (g.)	Boiling Point (°C)	Equivalent Weight	Remarks
1-4	8·4	125-151	84-88·8	Colourless liquids
5	6·7	151-151·8	88·2	Calc. for $C_8H_8O_2$ Equivalent weight 88·1
6-9	4·5	151·8-175	88·7-94	Decolourised bromine water
10-12	8·9	175-187	98·7-99·8	Decolourised bromine water. Mostly solid
13	4·2	187-193	99·9	Decolourised bromine water Mostly solid
14	4·2	193-195	99·6	Decolourised bromine water Mostly solid

The residue in the pot (5·4 g.), which was mostly crystalline but very high boiling, was combined with the residue (42 g.) of the preliminary distillation. Sublimation of this material in high vacuum (10 ^{4}mm.) gave a small amount of liquid acid, which was discarded, and a crystalline acid (6·6 g.), which was recrystallised from water to give large colourless needles, m.p. and mixed m.p. with anisic acid 184-184·5° (Found: C, 63·4; H, 5·5; Equivalent weight, 152, 155. Calc. for $C_8H_8O_3$: C, 63·2; H, 5·3%; Equivalent weight, 152). The *p*-bromophenacyl ester crystallised from aqueous ethanol in colourless plates, m.p. and mixed m.p. with an authentic sample of the *p*-bromophenacyl derivative of anisic acid, 153·5-154·5°.

Fraction 5 gave a *p*-bromophenacyl ester which crystallised in plates from aqueous methanol, m.p. and mixed m.p. with the *p*-bromophenacyl ester of *iso*-butyric acid 76·5-78° (Found: C, 50·7; H, 5·0. Calc. for $C_{12}H_{13}O_3$.Br: C,50·55; H, 4·6%).

Fractions 10-12 crystallised from water in small colourless crystals, m.p. 44-45° (literature 45° for angelic acid) (Found: Equivalent weight, 99·5. Calc. for $C_5H_8O_2$: 100·1). The *p*-bromophenacyl ester was crystallised from aqueous methanol, m.p. 68·5-69·5° (Found: C, 52·4; H, 4·25. $C_{13}H_{13}O_3Br$ requires: C,52·5; H,4·4%). Mixed m.p. of this ester with the corresponding ester of tiglic acid (m.p. 68·5-69·5°) was 55-58°.

Fraction 14 gave large colourless prisms from water, m.p. 64·5-65·5° (literature 64° for tiglic acid) (Found: Equivalent weight, 99·9. Calc. for $C_5H_8O_2$: 100·1). The *p*-bromophenacyl ester crystallised from aqueous ethanol in plates, m.p. 68·5-69·5° (literature gives 67·9°) (Found: C,52·7; H,4·3. Calc. for $C_{13}H_{13}O_3$ Br: C, 52·5; H, 4·4%).

The remaining fractions cited in the above table were shown to be mixtures of the identified acids.

The Free Acids

Fraction II was acidified with dilute sulphuric acid and extracted with ether. Evaporation of the solvent from the dried solution (Na_2SO_4) left a viscous, black tar (157 g.; 32·8% of the resin). This was treated in essentially the same way as the combined acid fraction and small amounts of anisic, *iso*-butyric and angelic acids were isolated. By far the largest portion of this material was a non-volatile black tar.

The Unsaponifiable Fraction

A crystalline precipitate of euryopsonol (7·4 g; m.p. 222-225°) was obtained on storing a solution of Fraction III (133 g.) in pure dry ether (2 l.). This was filtered off, and the filtrate chromatographed on alumina (2 kg.; activated at 350°) as shown in Table II.

TABLE II

Fraction	Vol. (l.)	Solvent	Weight (g.)	Remarks
1-7	8	dry ether	52·64	Liquids + crystals
8-13	6	wet ether	5·83	Viscous liquids + crystals
14-18	5	ether + 1% ethanol	26·50	Viscous liquids + crystals
19	1	ether + 1% ethanol	4·34	Gum. Rejected
20	5	ether + 1% ethanol	2·71	Gum + crystals
21-23	3	ether + 5% ethanol	7·53	Mostly crystals
24-25	2	ether + 10% ethanol	2·63	Mostly crystals
26-27	2	ether + 15% ethanol	0·94	Mostly crystals
28-29	2	ether + 15% ethanol	0·47	Gum. Rejected

Fractions 1-13 were combined and rechromatographed as described later. Fractions 14-18 were separately triturated with ether and the crystals of euryopsonol (m.p. 222-225°) filtered off (3·5 g.). The crystalline materials obtained on a similar trituration of fractions 20-27 were found to be mixtures of two or more substances.

Fractions 1-13 (*Table II*). To these fractions was added the liquid residues of fractions 14-18, which were obtained after the removal of the euryopsonol. The mixture (40 g.) in *n*-pentane (400c.c.) was filtered free of a small residue and then chromatographed on alumina (600 g.).

TABLE III

Fraction	Vol. (c.c.)	Solvent	Weight (g.)	Remarks
1-4	600	*n*-pentane	0·38	Colourless crystals
5-6	400	*n*-pentane	2·50	Gums. Rejected
7-13	1,400	*n*-pentane	4·59	Gums
14-22	1,800	*n*-pentane with increasing proportions of ether up to 100% for 23	10·16	Gums
23-32	2,000	Ether	6·80	Gums
33-43	2,200	Ether with increasing proportions of ethanol up to 50% for 40	10·15	Gums + traces of crystal
44-45	500	Ethanol	0·35	Gums. Rejected

Fractions 1-4 were combined and recrystallised many times from ethanol to yield colourless plates, m.p. 66·0-66·2° (Found: C, 85·35; H, 15·1; C-methyl, 2·0; Molecular weight (Rast), 450, 460. $C_{32}H_{66}$ requires: C, 85·2; H, 14·8; C-methyl, 3·3%; Molecular weight, 451). Long crystal spacing, 39·8Å. This places the length of the carbon chain at about C_{30}. Investigation of this minor constituent was not continued.

Fractions 5-22 (50·6 g.; from a larger scale chromatogram) were combined and fractionated in a spinning band column having an efficiency equal to about 15 theoretical plates at 1mm. It proved to be a very complex mixture, the bulk of the material (33 g.) boiling over the range 150-163°. The fraction b.p. 160-163° (16 g.) was solid and was separated, by fractional crystallisation from methanol, into two main products, m.p. 93-95° and m.p. 163-165°.

The substance, m.p. 93-95° was chromatographed in pentane solution on alumina, yielding as the main fraction a compound which crystallised in tablets from hexane, m.p. 105·5-106·5° (Found: C, 74·1; H, 8·9; OCH_3, 10·4, 10·5. $C_{18}H_{26}O_3$ requires: C, 74·5; H, 8·9; OCH_3, 10·7%). The substance, m.p. 163-165°, was recrystallised repeatedly from methanol but it could not be obtained pure, m.p. 163-165° (Found: C, 73·4; H, 8·8; OCH_3, 10·5. $C_{17}H_{24}O_3$ requires: C, 73·9; H, 8·7; OCH_3, 11·3%). The residue in the still pot was recrystallised several times from methanol to give colourless plates, m.p. 66-66·5°. This was the same (mixed m.p.) as the hydrocarbon above. No further pure materials could be isolated from any of the distillation fractions.

Fractions 23-43 (33 g.; from a larger scale chromatogram) were combined and fractionated in the spinning band still, at 1mm. pressure, to give three main fractions: (1) colourless, pleasant smelling oil, partly crystalline (5 g.), b.p. 75-100°; (2) viscous oil, which could not be crystallised (3·5 g.), b.p. 150-160°; (3) a waxy substance (4·5 g.), b.p. 190-200°. The greater part of the material remained as an undistillable tar. The waxy substance (b.p. 190-200°) was triturated with ether and the insoluble matter (1·3 g.) filtered off. This was shown (mixed m.p.) to be euryopsonol. The ethereal solution was evaporated to a small bulk, the crystals filtered off and recrystallised several times from *iso*-hexane to give colourless leaflets, m.p. 74-74·5° (Found: C, 81·0; H, 14·2; Molecular weight, 349 (Rast). Calc. for $C_{23}H_{48}O$: C, 81·1; H, 14·2%; Molecular weight, 341). The acetate was recrystallised from pentane at −30°, m.p. 55-55·5° (Found: C, 78·4; H, 13·1. Calc. for $C_{25}H_{50}O_2$: C, 78·5; H, 13·2%). This is probably *n*-tricosanol (literature m.p. 73·5-74·5°).

Experiments with Euryopsonol

It was purified by repeated crystallisation from benzene and finally methanol. It crystallised in large, almost colourless prisms, m.p. 230-232° (decomp.) Found: C, 72·6, 72·6, 72·3; H, 8·2, 8·1, 8·1; C-methyl, 6·1; Molecular weight (Rast), 216, 225; 12·50 and 9·70 mg. in ethanol absorbed 2·34 and 1·69c.c. H_2 at N.T.P. over $Pd/CaCO_3$ catalyst (2% Pd). $C_{15}H_{20}O_3$ (2 double bonds) requires: C, 72·5; H, 8·1; C-methyl, 6·05%: Molecular weight, 248; 2·25 and 1·75 c.c. H_2). $[\alpha]_D^{22}$, −36 (in chloroform). It absorbed 1·48 moles of perbenzoic acid per mol. after standing for 72 hours in perbenzoic acid solution. The epoxide could not be isolated in a pure condition.

The acetate was formed by heating with an excess of acetic anhydride on a water bath for several hours. After removing the excess acetic anhydride *in vacuo*, the acetate was recrystallised from ethanol (charcoal) as colourless needles, m.p. 196-198° (Found: C, 70·4, 70·4; H, 7·7, 7·9. $C_{17}H_{22}O_4$ requires: C, 70·3; H, 7·6%).

Euryopsonol did not form a semicarbazone but it gave a 2:4-dinitrophenylhydrazone, fine orange needles from ethyl acetate, m.p. 288·5-289° (Found: C, 59·5, 59·6; H, 5·85, 5·6; N, 12·8, 12·5. $C_{21}H_{24}O_6N_4$ requires: C, 58·9; H, 5·65; N, 13·1%).

The analyses were carried out in our Microchemical Department by Mr. F. W. G. Schöning and Mrs. V. M. Maritz.

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THE USE OF RADIOPHOSPHORUS IN THE INVESTIGATION OF PHOSPHATE AVAILABILITY IN TWO NATAL SOILS*

by

E. R. ORCHARD and W. J. FÖLSCHER

OPSOMMING

In die proef wat beskryf word, is tef in groot erdepotte gesaai met die oogmerk om die opname van fosfor in twee suur Natalse gronde te ondersoek. Vir hierdie doel is radioaktiewe superfosfaat gebruik. Daarbenewens is ook ander behandelings toegepas met die doel om moontlik die toeganklikheid van sowel die natuurlike as die kunsmis-fosfor te verbeter; dit is bekend dat die toeganklikheid van super maar laag is in die suur, ysterryke gronde wat tipies is van die Natalse misstreek.

Aangesien daar aanduidings is dat superfosfaat toenemend minder toeganklik word na toediening, is die proef ook bedoel om lig te werp op die invloed van hierdie tydsfaktor. In diè opsig was die proefbevindings nie beslissend nie maar bykomstige behandelings, veral die gebruik van landboukalk, het getoon dat die twee gronde baie uiteenlopend reageer, soos bewys deur die oesopbrengste en ook die opname van beide natuurlike en kunsmis-fosfor.

SUMMARY

An experiment is described in which teff was grown in large pots with the object of studying the uptake of phosphorus from two acid Natal soils. For this purpose, radiophosphorus-labelled superphosphate was used; the soils also received subsidiary treatments which, it was thought might improve the availability of both soil and fertilizer phosphorus. The availability of the latter is known to be poor in the acid ferruginous soils which are typical of the Natal mist belt.

Since there is some evidence that superphosphate becomes progressively less available with time once the fertilizer is applied to the soil, the experiment was at the same time designed to provide more critical evidence on the effect of this time factor. In this respect no clear-cut trend could be established from the experimental data but subsidiary treatments, particularly the use of lime, showed that the two soils reacted very differently as measured by yield and uptake of both soil and fertilizer phosphorus.

INTRODUCTION

The work of Williams[1] and others has shown that acid lateritic yellow earths from Natal possess a remarkably high capacity for rendering superphosphate insoluble. An earlier pot experiment by the authors, using various forms of phosphatic fertilizer, had also indicated that the amount of phosphate assimilated by a test crop grown on acid Natal soils, appeared to decrease as the time lapse between the date of applying the fertilizer and the date of sowing the crop, was increased. This suggested a progressive lowering of availability from the time of applying the fertilizer.

In order to shed more light on the effect of the time factor and also on the further problem of whether or not subsidiary soil treatments, including liming, might not enhance the availability of superphosphate, it was decided to conduct an experiment using radiophosphorus-labelled superphosphate.

In most agricultural work with radioactive superphosphate, the emphasis has been given to studies of a plant-physiological character; in the present work the tracer technique was used with the main object of elucidating certain soil problems so that the effect of treatments on yield and composition of the test crop was only of secondary importance. This report covers an investigation designed to study the effect of applying radioactive super at three different times before sowing and at sowing time on the availability of such phosphorus and also to measure the effect of lime, sulphate of ammonia and decomposing organic matter on the uptake of both soil and fertilizer phosphorus.

*From a paper read at the annual convention of the S.A. Chemical Institute held in Durban, July, 1953.

EXPERIMENTAL

Two soils were used: (a) a ferruginous yellowish red loam (pH5·1), of mixed shale and dolerite origin, from the College of Agriculture, Cedara; a soil which is subject to severe leaching during the rainy season in summer and is consequently deficient in exchangeable bases, particularly calcium and potassium, and (b) a doleritic grey-black clay (pH 5·7) from the Agricultural Experiment Station, Ukulinga, near Pietermaritzburg. The latter soil is not as severely leached as that from Cedara and it is classified as a sub-tropical black clay. It is relatively well supplied with bases particularly calcium. According to the method of Bray and Kurtz[2] the highly available absorbed and easily acid-soluble phospho us content was found to be 0·95 and 0·65 p.p.m. P for Cedara and Ukulinga soil respectively.

Forty large earthenware pots, each with a capacity of 50 lb. soil were filled in October, 1951, with each of the two soils. They were arranged in the open in a randomised block layout, comprising five treatments, each applied at four different times; there were two replications, making a total of eighty pots. The treatments were as follows:—

O = Control or no fertilizer.
S = 300 lb. super/ac. (2·5 g./pot).
SL = 300 lb. super+4 tons agricultural lime/ac. (66·6 g. lime/pot).
SM = 300 lb. super+4 tons organic matter/ac. (66·6 g. organic matter/pot).
SN = 300 lb. super+300 lb. sulphate of ammonia/ac. (2·5 g. S/A/pot of which half was applied at sowing and the remainder, one month later).

The super had a total P_2O_5 content of 17·3% and a specific activity of 891 μrd./mg. P on 27:12:1951. The organic matter consisted of finely ground paspalum grass with a P_2O_5 content of 142 mg./100 g.

The above treatments, collectively referred to as "fertilizer" treatments for convenience, were applied to the two soils at fortnightly intervals, viz:—

T_1—29:10:51; T_2—12:11:51; T_3—26:11:51; T_4—10:12:51. At the date of the first fertilizer application, the soil in all pots was brought to half the field capacity which was regarded as being sufficiently moist to permit all normal reactions and processes in the soil. The moisture content was maintained until the last application was made and the test crop was sown. The materials to be applied were thoroughly mixed with 30 lb. of soil which was then replaced in the pot and covered with 10 lb. of untreated soil so as to minimize contamination at the surface.

At the time of the last fertilizer application, the pots were all sown to teff, (*Eragrostis tef*, Unie-Bruin variety), and twenty days later they were uniformly thinned to 30 plants per pot. Throughout the growing period the pots were maintained as near as possible to the optimum moisture content and no leaching took place.

From the outset, plants on the Ukulinga soil grew much more rapidly and one month after sowing, their average height was 19·3 in. as compared with 11·2 in. of those on Cedara soil. This disparity later gradually disappeared until, at harvest time, they were practically equal. The superiority of the teff on soil from Ukulinga is reflected in the higher yields and in the fact that the plants matured a week earlier. The crop was harvested at the seed setting stage by cutting it one inch above soil level; all the material was immediately made oven-dry, weighed and milled prior to analysis. The crop on the Ukulinga soil was harvested 60 days after sowing and on the Cedara soil, a week later.

The material from individual pots was analysed; total phosphorus being determined by standard colorimetric methods, while fertilizer phosphorus, taken up by the plants, was measured electronically using M12 type liquid counters. Using these data it is possible to distinguish between phosphorus derived from the soil and that derived from the fertilizer.

TABLE I

The effect of Treatment on Yield and Uptake of Phosphorus.

Treatment		Dry matter yield grams	Total P taken up, mg. P	Soil P taken up, mg. P	Fertilizer P taken up, mg. P	Ratio. Soil P: Fert. P
Cedara Soil						
1	O1					
2	O2					
3	O3	95	89·7	89·7	—	—
4	O4					
5	S1	142	130·5	82·5	48·0	1·72
6	S2	135	127·4	79·5	47·9	1·66
7	S3	154	130·9	80·3	50·6	1·59
8	S4	174	149·2	97·6	51·6	1·89
9	SL1	178	186·3	119·5	66·8	1·79
10	SL2	122	140·8	84·7	56·1	1·51
11	SL3	174	209·6	143·5	66·1	2·17
12	SL4	192	227·7	161·8	65·9	2·46
13	SM1	174	162·5	103·1	59·4	1·74
14	SM2	128	139·3	91·6	47·7	1·92
15	SM3	169	169·0	106·9	62·1	1·72
16	SM4	160	161·3	107·6	53·7	2·00
17	SN1	158	147·4	87·4	60·0	1·46
18	SN2	167	150·2	94·6	55·6	1·70
19	SN3	194	170·1	111·9	58·2	1·92
20	SN4	196	165·3	108·5	56·8	1·91
Mean of 16 phosphate treats.		164	160·5	103·8	56·7	1·82
Ukulinga Soil						
1	O1					
2	O2					
3	O3	149	249·2	249·2	—	—
4	O4					
5	S1	152	302·8	221·9	80·9	2·74
6	S2	195	403·0	299·5	103·5	2·89
7	S3	169	311·5	230·6	80·9	2·85
8	S4	96	265·8	192·6	73·2	2·63
9	SL1	184	268·3	194·9	73·4	2·66
10	SL2	163	232·9	170·5	62·4	2·73
11	SL3	203	259·8	192·1	67·7	2·84
12	SL4	187	300·8	218·3	82·5	2·65
13	SM1	177	340·2	255·0	85·2	2·99
14	SM2	213	389·3	303·1	86·2	3·52
15	SM3	221	400·2	317·8	82·4	3·86
16	SM4	59	192·2	154·1	38·1	4·04
17	SN1	230	342·1	251·1	91·0	2·91
18	SN2	221	320·9	234·7	86·2	2·72
19	SN3	257	402·3	298·3	104·0	2·87
20	SN4	209	375·4	279·5	95·9	2·91
Mean of 16 phosphate treats.		183	319·2	238·4	80·8	2·99
S.E. % of GM		20·5	13·4	15·0	14·3	—
Sig. Dfce. between treatments:						
at 5% level		57·5	61·2	51·7	20·1	—
at 1% level		68·9	73·3	62·0	24·1	—

Table I shows the dry matter yields, total phosphorus, soil phosphorus and fertilizer phosphorus assimilated as well as the ratio, soil P: fertilizer P in the plants

at harvesting. The suffix to treatments indicates the time of applying the fertilizer. With the exception of the data for the ratios and the means shown opposite the (dummy) control treatments 1-4, individual figures in the body of the table represent treatment totals i.e. the sum of two replicates in each case although the determinations and the subsequent statistical analysis were conducted on material from individual pots.

PRESENTATION OF RESULTS

The statistical analysis of the data has by no means been exhaustive and only the most notable comparisons will be discussed. Only data in respect of main effects and the interaction, Fertilizer × Time of application, will be presented for the two soils as these hold the main interest.

A.—Yield of Dry Matter, (g.)

TABLE II

Fertilizer treatment × Time of application.

Treatment	O	S	SL	SM	SN	*Totals*
Cedara Soil						
Time 1	96	142	178	174	158	748
„ 2	102	135	122	128	167	654
„ 3	88	154	174	169	194	779
„ 4	95	174	192	160	196	817
Totals	381	605	666	631	715	2,998
Ukulinga Soil						
Time 1	178	152	184	177	230	921
„ 2	138	195	163	213	221	930
„ 3	175	169	203	221	257	1,025
„ 4	106	96	187	59	209	657
Totals	597	612	737	670	917	3,533

Least significant differences:	5% *level*	1% *level*
Body of table	57·5	68·9
Marginal totals	114·9	137·7

Conclusions:

The yield from Ukulinga soil was significantly better, by approx. 18%, than that from Cedara soil.

Cedara: (a) There were no significant differences between fertilizer treatments but all, including super alone, were superior to the untreated soil.

(b) $T_4, T_3 > T_2$.

Ukulinga: (a) Only where sulphate of ammonia or lime was applied in addition to super was the yield superior to the control. The response to super alone was not significant; SN > SL > O.

(b) $T_3, T_2, T_1 > T_4$.

B. Total Phosphorus Taken Up, (mg. P).

TABLE III

Fertilizer treatment × Time of application.

Treatment	O	:	S	SL	SM	SN	:	*Totals*
Cedara Soil								
Time 1	96·8	:	130·5	186·3	162·5	147·4	:	723·5
„ 2	85·5	:	127·4	140·8	139·3	150·2	:	643·2
„ 3	90·4	:	130·9	209·6	169·0	170·1	:	770·0
„ 4	85·9	:	149·2	227·7	161·3	165·3	:	789·4
Totals	358·6	:	538·0	764·4	632·1	633·0	:	2,926·1
Ukulinga Soil								
Time 1	285·4	:	302·8	268·3	340·2	392·1	:	1,538·8
„ 2	231·0	:	403·0	232·9	389·3	320·9	:	1,577·1
„ 3	267·9	:	311·5	259·8	400·2	402·3	:	1,641·7
„ 4	212·5	:	265·8	300·8	192·2	375·4	:	1,346·7
Totals	996·8	:	1,283·1	1,061·8	1,321.9	1,440·7	:	6,104·3

Least significant differences:	5% *level*	1% *level*
Body of table	61·2	73·3
Marginal totals	122·3	146·6

Conclusions:

The crop took up more than twice as much phosphorus from Ukulinga as from Cedara soil in spite of the fact that the difference in dry matter yield was only 18%, (see Table II).

Cedara: (a) All fertilizer treatments were superior to the control.

(b) Super in the presence of lime was superior to super alone so that liming appears to improve phosphate assimilation.

(c) $T_3, T_4 > T_2$.

Ukulinga: (a) Except where lime was applied, all fertilizer treatments are superior to the control.

(b) Lime in the presence of super significantly depressed the total amount of phosphate assimilated in comparison with super given alone, a result which contrasts strongly with findings on Cedara soil. Where sulphate of ammonia was given in addition to super, the uptake was significantly better than with super alone.

(c) $T_1, T_2, T_3 > T_4$.

C. Soil Phosphorus Taken Up, (mg. P).

TABLE IV

Fertilizer treatment × Time of application.

Treatment	O	S	SL	SM	SN	*Totals*
Cedara Soil						
Time 1	96·8	82·5	119·5	103·1	87·4	489·3
„ 2	85·5	79·5	84·7	91·6	94·6	435·9
„ 3	90·4	80·3	143·5	106·9	111·9	533·0
„ 4	85·9	97·6	161·8	107·6	108·5	561·4
Totals	358·6	339·9	509·5	409·2	402·4	2,019·6
Ukulinga Soil						
Time 1	285·4	221·9	194·9	255·0	251·1	1,208·3
„ 2	231·0	299·5	170·5	303·1	234·7	1,238·8
„ 3	267·0	230·6	192·1	317·8	298·3	1,306·7
„ 4	212·5	192·6	218·3	154·1	279·5	1,057·0
Totals	996·8	944·6	775·8	1,030·0	1,063·6	4,810·0

Least significant differences:	5% *level*	1% *level*
Body of table	51·7	62·0
Marginal totals	103.3	123·9

Conclusions:

The test crop took up 138% more soil phosphorus from the Ukulinga soil than from the Cedara soil. The method of Bray and Kurtz therefore appears to be inadequate as a means of distinguishing between the amounts of readily available phosphorus in these two soils.

Cedara: (a) Only in the presence of lime did the application of super lead to an improved uptake of soil phosphorus. In this respect, super alone was no better than the control in spite of the fact that there was a good response as measured by crop yield (see Table II).

(b) $T_4 > T_2$.

Ukulinga: (a) In sharp contrast with findings on the Cedara soil, the use of lime significantly depressed the uptake of soil phosphorus as compared with all other treatments including the control.

(b) Sulphate of ammonia in the presence of super significantly improved the uptake of soil phosphorus as compared with super alone.

(c) As on Cedara soil, super alone showed no advantage over the control.

(d) $T_1, T_2, T_3 > T_4$.

D. Superphosphate Phosphorus Taken Up, (mg. P.)

TABLE V

Fertilizer treatment × Time of application.

Treatment	O	S	SL	SM	SN	*Totals*
Cedara Soil						
Time 1	—	48·0	66·8	59·4	60·0	234·2
„ 2	—	47·9	56·1	47·7	55·6	207·3
„ 3	—	50·6	66·1	62·1	58·2	237·0
„ 4	—	51·6	65·9	53·7	56·8	228·0
Totals	—	198·1	254·9	222·9	230·6	906·5
Ukulinga Soil						
Time 1	—	80·9	73·4	85·2	91·0	330·5
„ 2	—	103·5	52·4	86·2	86·2	338·3
„ 3	—	80·9	67·7	82·4	104·0	335·0
„ 4	—	73·2	82·5	38·1	95·9	289·7
Totals	—	338·5	286·0	291·9	337·1	1,293·5

Least significant differences:	5% *level*	1% *level*
Body of table	20·1	24·1
Marginal totals	40·1	48·3

Conclusions:

The test crop recovered significantly more, (43%), superphosphate phosphorus from Ukulinga soil than from Cedara soil.

Cedara: (a) The use of lime significantly improved the uptake of phosphorus from the added super while the effects of sulphate of ammonia and organic matter were nearly significant.

(b) Time of application had no effect on the uptake of fertilizer phosphorus.

Ukulinga: (a) As was the case with total phosphorus and soil phosphorus, lime in the presence of super also depressed, significantly, the amount of superphosphate phosphorus taken up by the crop as compared with super alone. Organic matter had a similar depressing effect.

(b) $T_1, T_2, T_3 > T_4$.

E. Ratio of Soil P : Superphosphate P Taken up by the Crop.

The mean ratio for all fertilizer treatments on Cedara soil was 1·82 as against 2·99 for Ukulinga soil, (see Table I). No detailed statistical analysis of these ratios was carried out but on neither soil did treatment appear to have much effect on the ratio.

F. Recovery of Phosphorus from Added Superphosphate.

Wherever super was applied, the dressing amounted to 189 mg. P per pot. The average recovery from this fertilizer dressing was 28 mg. and 40 mg. P or 15% and 22% for Cedara and Ukulinga soil respectively. In spite of the poorer recovery from Cedara soil there was nevertheless a good yield response to added phosphate, whereas there was no response to super alone on the Ukulinga soil, (see Table II). This may be taken as evidence in support of the view that superphosphate is rendered particularly unavailable in the acid leached soils of which Cedara is representative.

The recovery values mentioned above are remarkably high and should probably be ascribed to the conditions under which the experiment was conducted. The teff formed a dense root mat in the pots and could therefore exhaust the potential resources to an exceptional extent. Under field conditions the recovery is unlikely to be as high. It should be pointed out that with the Neubauer laboratory technique for assessing available phosphate, whereby a dense stand of seedlings is used to exhaust a relatively small quantity of soil, the seedlings are able to extract more phosphorus per unit weight of soil in 18 days than is possible for agronomic crops growing to maturity on the same soil under field conditions.

On a soil of pH 6·1 and with superphosphate applications ranging from approximately 50-200 lb. per acre to which the test crop, (maize), responded handsomely, van Garderen and van der Walt[3] recovered only 5% in the above-ground portion of the crop. In an earlier experiment on a similar but more fertile soil, van Garderen and others[4] recovered only 2% of the phosphorus added. Similarly Pearse and Stein[5] using comparatively heavy dressings of superphosphate on both the red and the black tobacco soils of Rustenburg, Transvaal, demonstrated recoveries ranging from 4·7% to 11·8% ,in favour of the black soil which is similar in many respects to the Ukulinga soil.

It is thus feasible to ascribe the failure to demonstrate any logical or consistent trend in the effect of the time of application on the recovery of superphosphate by teff grown in pots, to the artificial conditions of the experiment. The abnormally high recovery resulting from the intensive root development of the crop seems to have masked the effect of the time factor. It would seem that this important question and many other soil fertility problems can be satisfactorily investigated only by means of field experimentation.

CONCLUSIONS

(a) *Soils.* Dry matter yields and the amounts of both soil and superphosphate phosphorus taken up were significantly higher on Ukulinga than on Cedara soil.

(b) *Time of application.* On Ukulinga soil, applications of super 2-6 weeks before sowing resulted in better yields and a higher uptake of both soil and fertilizer phosphorus than the application at sowing time.

On Cedara soil the uptake of fertilizer phosphorus was little affected by time of application, but both yield and uptake of soil phosphorus were higher when applications were made at sowing time.

(c) *Fertilizer effects.*

(i) Super increased dry matter yields on Cedara but not on Ukulinga soil. On neither soil did super applications improve the uptake of soil phosphorus.

(ii) The use of lime in the presence of super on Cedara soil increased the uptake of both soil and superphosphate phosphorus in spite of the fact that there was only a slight (non-significant) increase in yield as compared with super alone. On Ukulinga soil, lime increased the yield significantly but at the same time depressed the uptake of both soil and superphosphate phosphorus significantly.

(iii) Sulphate of ammonia increased the yield and the uptake of soil phosphorus on both soils but these effects were significant only on Ukulinga soil. There are indications (not sig.) that sulphate of ammonia also increased the amount of fertilizer phosphorus taken up on both soils.

(iv) The use of organic matter in conjunction with superphosphate did not appear to offer any particular advantage.

(d) *Ratio of soil P : superphosphate P taken up.* This ratio is considerably higher for Ukulinga soil than for Cedara soil indicating a superior availability of soil phosphorus on Ukulinga soil.

(e) *Recovery of phosphorus from added superphosphate.* Of the phosphate applied, 22% was recovered from Ukulinga soil as against 15% from Cedara soil. This difference may be due to more complete fixation of phosphorus in unavailable forms in Cedara soil but the question requires further investigation.

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"THE 2-METHYL-3-HYDROXY-4-METHOXYPENTANE-3-ACIDS"

by

L. J. DRY

OPSOMMING

2-Metiel-4-metoksiepentaan-3-on (I) word met asetileen gekondenseer en die produk word gehidrateer en ge-oksideer tot 'n skynbare mengsel van ±-*treo*-en ±-*eritro*-2-metiel-3-hidroksie-4-metoksiepentaan-3-karboksielsure, VI en VII onderskeidelik.*

2-Metielpent-3-ien-3-karboksielsuur (VIII) word behandel om metoksiekwik en metoksiebroom afleidingsprodukte te gee en die is omgeset in α-hidroksiesure.

Heliotriensuur is nie uit die produkte afgeskei nie.

SUMMARY

2-Methyl-4-methoxypentan-3-one (I) is condensed with acetylene and the product hydrated and oxidised to yield an apparent mixture of (±)-*threo*-and (±)-*erythro*-2-methyl-3-hydroxy-4-methoxypentane-3-carboxylic acids, (VI) and (VII) respectively.*

2-Methylpent-3-ene-3-carboxylic acid (VIII) is methoxymercurated and methoxybrominated and the products converted to α-hydroxy-acids.

Heliotrinic acid is not isolated from products obtained.

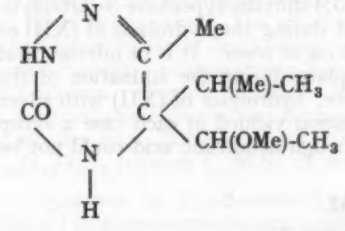
With a view to the synthesis of heliotrinic acid, m. p. 93—95°, $[\alpha]_D$ −12°, which has been obtained by the hydrolysis of heliotrine[1] and isoheliotrine[2], various syntheses of the 2-methyl-3-hydroxy-4-methoxypentane-3-carboxylic acids have been investigated. The structure of heliotrinic acid was elucidated by Menshikov[3], while Adams and van Duuren[4] have recently shown that this acid is stereochemically related to trachelantic acid. Heliotrinic acid possesses therefore the *threo*- configuration[6] (VI).

Condensation of (±)-2-methyl-4-methoxypentan-3-one (I) with acetylene, followed by hydration and oxidation of the product, led to an apparent mixture (IV) of (±)-*threo*- and (±)-*erythro*-2-methyl-3-hydroxy-4-methoxypentane-3-carboxylic acids.

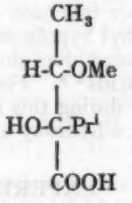
$$CH3.CHMe.CO.CH(OMe).CH_3 \longrightarrow CH_3.CHMe.C(OH)R.CH(OMe).CH_3$$

(I)

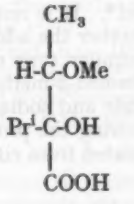
(II), R=—C:CH
(III), R=—$COCH_3$
(IV), R=—CO_2H



(V)



(VI)



(VII)

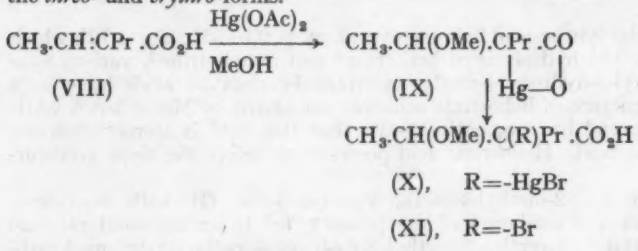
The ketone (I) obtained by the oxidation of heliotrinic acid[3], has been synthesised in poor yield from α-methoxypropionitrile by Wallace and Henze[5]. For this study (I) has been prepared in good yield from α-methoxypropionitrile and less satisfac-

*The stereochemical designations refer to the vertically-printed four-carbon chain in formulae and VII. See reference 6.

torily from α-methoxypropionyl chloride according to the method of Gilman and Nelson.[7] The semicarbazone of (III) could be isolated only in a dehydrated form, ring closure to an unsymmetrical triazine (V) having probably occurred.

The acids (IV) were obtained as a non-crystallisable syrup. Crystallised from acetone, the morphine salts had m.p. 158-164°, recrystallisation leading gradually to 168°. Mixtures of these morphine salts with that of the (±)-*erythro*-acid (VII), the synthesis of which in these laboratories is being recorded elsewhere, always showed a rise in the melting point, indicating that (IV) contained the (±)-*erythro*-acid (VII), while analysis showed the absence of non-isomeric material. Demethylation of (IV) yielded an acid mixture, m.p. 122-132°, which with (±)-*erythro*-2-methyl-3:4-dihydroxypentane-3-carboxylic acid[6], m.p. 150°, gave a rise in melting point to 135-142°.

Methoxymercuration of 2-methylpent-3-ene-3-carboxylic acid[6] (VIII) yielded the *anhydro*-adduct (IX). Addition of bromine to a solution of (IX) in aqueous potassium bromide caused precipitation of the 3-mercuribromo-acid (X) and resulted in a poor yield of the 3-bromo-acid (XI). Hydrolysis of (XI) gave a syrup showing the characteristics of an α-hydroxy-acid, but again a crystalline acid could not be isolated. By analogy with the production of a mixture of diastereoisomeric α-bromo-β-methoxybutyric acids from crotonic acid[8], (XI) probably contained a mixture of the *threo*- and *erythro*-forms.



The methoxybromination of (VIII) may be expected to proceed by either *cis*- or *trans*-addition to yield a single disastereoisomer as chief or sole product[9], and has been described by Adams and van Duuren.[4] These authors failed to derive from the resulting 3-bromo-4-methoxy-acid (XII) the corresponding 3-hydroxy acid, and obtained instead by hydrolysis with potassium carbonate or silver oxide or by amination and hydrolysis, a product which they concluded to be the 3-methoxy-4-hydroxy-acid. The latter on demethylation gave a 3:4-dihydroxy-acid, m.p. 150°, which proved to be identical with (±)-*erythro*-2-methyl-3:4-dihydroxypentane-3-carboxylic acid[6]. It is not clear whether inversion occurred during the hydrolysis of (XII) or whether the addition of methyl hypobromite was *cis* or *trans*. It is of interest that a similar type of rearrangement does not take place during the amination of the α-bromo-β-methoxybutyric acids[8 9]. Furthermore, hydrolysis of (XII) with silver oxide and sodium carbonate during this investigation yielded in each case a syrup showing the properties of an α-hydroxy acid, although heliotrinic acid could not be isolated from either product.

EXPERIMENTAL.

(±)-2-*Methyl*-4-*methoxypentan*-3-*one*.

(a). (±)-α-Methoxypropionic acid, b.p. 103-106°/24 mm., was prepared in 84% yield from methyl (±)-α-chloropropionate without isolating the intermediate methyl α-methoxypropionate, by the method of Niemann, Benson and Mead[10]. The p-*phenylphenacyl* ester, m.p. 109°, crystallised in shiny laminae from benzene-light petroleum (Found: C, 72·5; H, 6·1; OCH_3, 10·0. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1; OCH_3, 10·4%). (±)-αMethoxypropionyl chloride, b.p. 66-74°/230 mm., was derived

in 73% yield from the acid by dropwise addition of the latter during one hour to thionyl chloride at 50° and fractional distillation of the reaction mixture. An ethereal solution of *iso*propyl magnesium bromide (from 40 g. magnesium) was cooled to −5° and powdered anhydrous cadmium chloride (183 g.) added during 1 hour with vigorous stirring. After stirring for a further 30 minutes, (±)-α-methoxypropionyl chloride (74 g.) in ether (350 ml.) was added with stirring at such a rate that the temperature of the reaction mixture did not exceed −1°, and the whole left in a freezing bath for 15 hours. The organocadmium complex was hydrolysed with ice and cold 2N sulphuric acid and the product, obtained in the usual way, distilled to yield (±)-2-methyl-4-methoxypentan-3-one (24 g., 30·5%), b.p. 65-75°/40 mm., while a high-boiling fraction (21·0 g.), b.p. 140-160°/40 mm., was also obtained. The *semicarbazone*, m.p. 145-146°, crystallised in prisms from water. (Found: C, 51·5; H, 9·05; N, 22·8; OCH_3, 16·2. $C_8H_{17}N_3O_2$ requires C, 51·35; H, 9·2; N, 22·5; OCH_3, 16·6%).

(b). (±)-αMethoxypropionitrile (25·7 g.) in ether (30 ml.) was added with stirring to an ethereal solution of *iso*propylmagnesium bromide (from 12 g. magnesium) at a rate maintaining gentle refluxing. After 18 hours at room temperature the complex was hydrolysed with iced 2N sulphuric acid and the ketone (27 g., 69%), b.p. 63-66°/37 mm., isolated as before. The semicarbazone, m.p. 144-146°, showed no depression with that prepared in (a).

(±)-2*Methyl*-3-*ethynyl*-4-*methoxypentan*-3-*ol*. A solution of potassium (22 g.) in *tert*-butanol (213 g.) and ether (100 ml.) was cooled to 10°, a strong jet of pure acetylene passed through and a solution of (±)-2-methyl-4-methoxypentan-3-one (63·5 g.) in ether (100 ml.) added dropwise with stirring during 1 hour. The reaction mixture was allowed to attain room temperature and acetylene was passed with stirring for 4 hours. The solution was poured into 1·15 N sulphuric acid (700 ml.), the mixture shaken vigorously, cooled to 0° and the ethereal layer separated. The aqueous layer was extracted twice with ether, the combined ether layers washed with 10% sodium chloride, dried over sodium sulphate and fractionally distilled to yield (±)-2*methyl*-3-*ethynyl*-4-*methoxypentan*-3-*ol* (59 g., 75%), b.p. 101-103°/40 mm., as a colourless liquid with a characteristic mint odour. (Found: C, 68·9; H, 9·9; OCH_3, 18·1. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3; OCH_3, 19·9%). A crystalline mercury compound could not be prepared.

(±)-2-*Methyl*-3-*acetyl*-4-*methoxypentan*-3-*ol*. The ethynyl carbinol (66·5 g.) was added dropwise to a boiling solution of mercuric oxide (10 g.) in 2N sulphuric acid (350 ml.) during 20 minutes and the mixture refluxed for a further hour, when some tarry material as well as some mercury was formed. The mixture was steam-distilled, the distillate made strongly alkaline with potassium carbonate and the supernatant oil taken up in ether. The alkaline layer was extracted with ether, the combined ether layers washed, dried over magnesium sulphate and distilled to yield (±)-2-*methyl*-3-*acetyl*-4-*methoxypentan*-3-*ol* (47 g., 63%) as a colourless liquid, b.p. 102-107°/35 mm. (Found: C, 62·2; H, 10·4. $C_9H_{18}O_3$ requires C, 62·05; H, 10·4%). A semicarbazone derivative, formed in aqueous pyridine, crystallised from benzene in needles, m.p. 218° (decomp.). (Found: C, 56·3; H, 8·8; N, 19·7; OCH_3, 16·7. $C_{10}H_{19}O_2N_3$ requires C, 56·3; H, 9·0; N, 19·7; OCH_3, 14·5%).

Oxidation of (±)-2-*methyl*-3-*acetyl*-4-*methoxypentan*-3-*ol*. Solutions of iodine (216 g.) in aqueous potassium iodide (258 g. in 1·5 l.) and sodium hydroxide (69 g.) in water (750 ml.) were added alternately to a mixture of the ketone (30 g.) and water (300 ml.) and the whole shaken vigorously after each addition. Formation of iodoform was rapid but incomplete, a heavy, unstable yellow oil being simultaneously formed. The supernatant solution was treated with a slight excess of sulphur dioxide, made alkaline with potassium carbonate and evaporated under reduced pressure to a small volume. The concentrate was acidified with 6N hydrochloric acid and the derived filtrate, freed of sulphur dioxide by aeration, extracted with chloroform. The chloro-

form extracts were washed twice with small volumes of saturated sodium chloride, dried over anhydrous sodium sulphate and evaporated to leave a syrupy acid residue (2·8 g.) containing some sulphur. The residue was dissolved in aqueous potassium carbonate, the sulphur extracted with carbon disulphide and the purified acid (2·0g.) isolated as before. No crystallisation occurred after desiccation for 12 months. The morphine salts, m.p. 158-164°, crystallised from moist acetone and showed a rise, 164-184°, with the salt of the (±)-*erythro*-acid (VII). Recrystallisation from the same solvent yielded a product, m.p. 163-166°, (Found: C, 62·5; H, 7·9; OCH_3, 6·5. $C_{25}H_{35}O_7N.H_2O$ requires C, 62·6; H, 7·8; OCH_3, 6·5%) also showing a rise with the salt of (VII), as did the products from further recrystallisations.

Demethylation procedure. The methoxy-acid (30 mg.) was heated to 100° with 48% hydrobromic acid (5 ml.) for 2 hours, the solution diluted somewhat and extracted with ether. The washed and dried ether extracts were evaporated and the residue sublimed at 90°/0·5 mm.

Methoxymercuration of 2-methylpent-3-ene-3-carboxylic acid. A mixture of 2-methylpent-3-ene 3-carboxylic acid (5 g.), methanol (55 ml.) and mercuric acetate (12·5 g.) was warmed to 55° until a clear solution resulted. Nitric acid (0·2 g.) was added and the mixture set aside at room temperature for 48 hours while anhydro-*2-methyl-3-mercurihydroxy-4-methoxypentane-3-carboxylic acid* (10 g.) gradually separated in large prisms. Fine prisms were obtained from chloroform-ethyl acetate. (Found: C, 26·9; H, 4·3; OCH_3, 8·6; Hg, 55·7. $C_8H_{14}O_3Hg$ requires C, 26·8; H, 3·9; OCH_3, 8·65; Hg, 55·9%).

Bromination of anhydro-*2-methyl-3-mercurihydroxy-4-methoxypentane-3-carboxylic acid.* To a solution of the *anhydro*-compound (34·7 g.) in potassium bromide (36 g.) and water (400 ml.) was added with stirring a solution of bromine (16·5 g.) in potassium bromide (24 g.) and water (200 ml.). Absorption of bromine was immediate and was accompanied by precipitation of *2-methyl-3-mercuribromo-4-methoxypentane-3-carboxylic acid* which crystallised in prisms, m.p. 108-109°, from ethyl acetate-light petroleum (Found: C, 22·3; H, 3·8; Br, 18·2. $C_8H_{15}O_3HgBr$ requires C, 21·9; H, 3·4; Br, 18·2%). The latter redissolved slowly and incompletely as the addition of bromine was continued. The supernatant solution was extracted with ether to remove a considerable quantity of acidic lachrymatory material, acidified with 65% hydrobromic acid and extracted with ether. The dried ether extracts yielded an oily bromo-acid (1·5 g.) which upon hydrolysis with potassium carbonate yielded a syrupy product giving an intense yellow colouration with ferric chloride. Bromination at 0° and in sunlight led to a lower yield of the bromo-acid, while bromination in chloroform or ethyl acetate was likewise unsatisfactory.

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STUDIES OF SOME PHYSICAL PROPERTIES OF SOUTH AFRICAN COALS

by

P. G. SEVENSTER

OPSOMMING

Die interne oppervlaktes van tipiese Sud-Afrikaanse steenkoolsoorte is volgens die benattingshittemetode van die B.C.U.R.A. bepaal. Die waardes word vergelyk met waardes wat bereken is deur die rekenmetodes van Brunauer, Emmett en Teller en van Harkins en Jura op steenkool-water isoterms toe te pas.

'n Metode word beskryf om die struktuurveranderings van steenkool by verskillende temperature vas te stel.

'n Metode word beskryf om die ware digtheid van steenkool te bepal, en 'n verband tussen die ware digtheid en die waterstofgehalte van Suid-Afrikaanse steenkoolsoorte word aangetoon.

Waardes vir porieëvolumes en porieëdiameters, bereken uit ware-en partikeldigthede, word aangegee.

Grootteverdeling van makroporiee van steenkool, bepaal met hulp van 'n hoedruk-porositeitsmeter, word bespreek.

SUMMARY

The surface areas of some South African coals are determined by means of the B.C.U.R.A.'s heat of wetting method and the results compared with values obtained by applying the methods of evaluation of Brunauer, Emmett and Teller and of Harkins and Jura to coal-water isotherms.

A method for studying the structural changes in coal at various temperatures is given.

A method is given for determining the density of coal and a relationship is established between the true density and hydrogen content of South African coals.

Pore volumes and pore diameters calculated from density data are given.

Macropore size distribution of coals, determined by means of a high pressure porosimeter, is discussed.

INTRODUCTION

The spontaneous heating of coal which may culminate in combustion has formed the subject of many studies. Despite the introduction of effective safety measures the mechanism of spontaneous heating is not clear. It is, of course, well known that spontaneous heating is bound up with the reaction of coal with oxygen and it is generally accepted that the surface of the coal exposed to oxygen is an important factor.*

Only recently, however, has interest been shown in the fine structure of coals which determines their available surface, e.g. their porosity, their pore volumes and pore size distribution. It appears likely that the smallest pores will play an important role in slow reactions, such as those occurring during weathering and slight but persistent spontaneous heating, while the larger capillaries will be of greater significance in rapid reactions such as combustion.

As spontaneous heating is ultimately due to chemical reactions, any investigation of surface properties must be supplemented by a study of activation energies of reactions occurring at these surfaces and of gaseous reaction products that result from at least some of these reactions.

This paper will, however, be confined to the determination of some physical properties of typical South African coals.

DETERMINATION OF SURFACE AREA

The heat of wetting method[2] and B.E.T. method[3] have been used to determine the surface area of coals and carbonaceous solids. Malherbe[4] and van Krevelen[5] have concluded that the heat of wetting method overestimates the surface area of

*In 1913 Winmill[1] established a dependence of oxygen absorption upon specific surface of coal, but his conclusion was based on limited experimental data.

coals. Their findings have given rise to controversy[6,7,8,9,10] the most important result of which, from the point of view of the present investigation, is the conclusion of Maggs[9] that the difference in values obtained by the two methods is probably due to a reduced accessibility of the internal surface of a coal at low temperature, brought about by structural changes. Evidence in support of this conclusion has also been obtained in the course of this study.

In seeking some correlation between surface area and spontaneous heating it is necessary to determine surface areas at temperatures where spontaneous heating is normally observed, *i.e.* at atmospheric and higher temperatures.

Emmett[11] and Gregg[12] have developed methods by which the absolute surface area of a solid may be calculated from adsorption isotherms obtained at room temperature. Values obtained by the heat of wetting method are stated to be in close agreement[13] with results obtained by these methods. Methanol has, however, been used in all these determinations. Coal expands when it adsorbs methanol and the high values obtained for surface area by means of measurements of the heat of wetting in methanol may, in part, be attributed to this swelling.

Since water causes relatively little swelling of coal, (about 2 per cent. by volume as against 16 per cent. in methanol[14]) and the question of chemical reaction is ruled out, it was thought advisable to use water adsorption data obtained at room temperature to calculate the surface area, and to provide a check on the heat of wetting method. Two methods of calculation, the B.E.T. method and a method developed by Harkins and Jura[15] were applied to the isotherms.

A. Determination of Surface Area by the Heat of Wetting Method.

When a solid is immersed in a liquid the heat evolved (H) is given by

$$H = c\,S \qquad (1)$$

where S is the surface area and c a constant. S can therefore be determined by measurement of H, provided c is known. The value of the constant c for carbon and coal derived from the work of Bangham[16] and Maggs[13] is 0·1 cal. m^{-2}

Experimental Procedure.

The sample is stored and ground under water to minus 60 mesh B.S.S. Finer grinding creates new surface but the contribution of this surface to the total surface is negligible[2].

The coal is superficially dried by pressing between sheets of blotting paper and then dried in nitrogen for half an hour at 105°C.

A 5 g. sample of coal is used in the determination.

The sample bulb, about 26 mm. in diameter, is fused to a glass tube (8 mm. in diameter and 15 cm. long) having a ground glass joint at its upper end. In order to facilitate breaking in the calorimeter, care is taken that there is no surplus glass at the lower end of the bulb and this is also blown out to a hemisphere of about 10 mm. diameter.

After the sample has been placed in a weighed bulb the lower end of the tube is drawn out to about 3 mm. diameter to facilitate fusing off later. The bulb is attached to a high vacuum system and evacuated while the sample is heated to 120°C. Six samples are evacuated simultaneously by attaching the sample bulbs to a suitable manifold which is fused on to the vacuum system. After a pressure of 10^{-5} mm. mercury has been attained, (usually after about 16 hours pumping), the bulb is sealed. The bulb and the sealed off portion of the connecting tube are then weighed and the weight of the dry evacuated sample is determined.

Calorimetric Determination.

The calorimeter used is illustrated in Fig. 1. The heat capacity of this calorimeter has been substantially decreased by the elimination of the separate stirrer and breaking rod which form part of the more conventional type of calorimeter used for heat of wetting determinations. The sample bulb (B) which is attached to

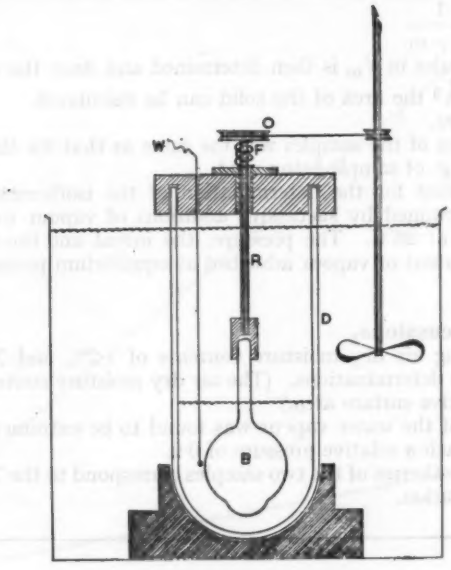

FIGURE 1

the stirrer shaft (R) by means of a piece of rubber tubing, is broken under methanol in a calorimeter of known water equivalent by a slight tap on the pulley (O). The bulb will return to its normal position by the action of the soft coil spring (F) inserted between the pulley and brass bush (A). The temperature change is measured by means of a thermistor and sensitive resistance bridge.

B. **Determination of Surface Area by Adsorption of Water Vapour at Room Temperature.**

Evaluation by the Method of Harkins and Jura.

The experimental data obtained from the adsorption of water vapour on coal at 25°C. are represented graphically by plotting the logarithm of the relative pressure $\left(\frac{P}{P_o}\right)$ against the reciprocal of the square of the volume adsorbed $\left(\frac{1}{V^2}\right)$. If the adsorbed vapour film forms a condensed phase in a certain pressure range the plot will exhibit a straight line relationship in that pressure range. The surface area S of the solid is given by the equation

$$S = k\, m^{\frac{1}{3}} \qquad (2)$$

where m is the numerical value of the slope of the linear portion of the curve and k a constant for a given adsorption vapour at a given temperature. The value for water at 25°C. is $3{\cdot}83^{15}$.

Evaluation by the B.E.T. Method.

Shortly, the method consists of plotting the relative pressure against $\frac{P/P_o}{V(1 - P/P_o)}$ in the pressure range 0·05 to 0·35. If the plot is a straight line the intercept (i) and the slope (m) are determined and the monolayer capacity (V_m) is calculated from:—

$$V_m = \frac{1}{i + m} \qquad (3)$$

The number of molecules in V_m is then determined and since the area of one water molecule is 10·5 sq. Å^2 the area of the solid can be calculated.

Experimental Procedure.

The pre-treatment of the samples was the same as that for the heat of wetting experiments, about 2 g. of sample being used.

The apparatus used for the determination of the isotherms is conventional. The isotherm is determined by successive additions of vapour to the coal sample which is maintained at 25°C. The pressure, the initial and the final volumes are measured and the amount of vapour adsorbed at equilibrium pressure is then calculated.

C. Results and Discussions

Two coals, having air dry moisture contents of 1·2% and 7·5% respectively were chosen for these determinations. (The air dry moisture content provides some indication of the relative surface area.)

The adsorption of the water vapour was found to be extremely slow, requiring up to four days to reach a relative pressure of 0·9.

The adsorption isotherms of the two samples correspond to the Type II isotherms of the B.E.T. classification.

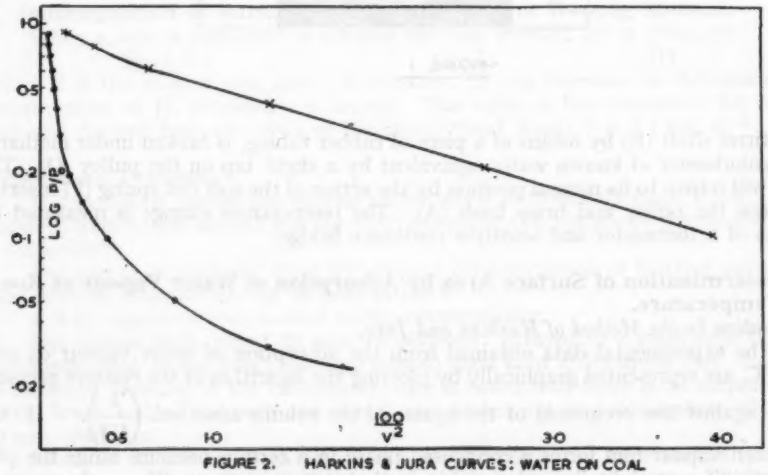

FIGURE 2. HARKINS & JURA CURVES: WATER ON COAL
SAMPLE 44C ••••
SAMPLE 268B ××××

In Figure 2 the isotherms are plotted according to the method of Harkins and Jura. The curves exhibit a linear relationship in the region $\frac{P}{P_o} \sim 0{\cdot}2$. This linear relationship is considered to represent a condensed film on the solid. In the case of sample no. 268B, two condensed phases are present. The slope of the phase appearing at the lower pressure was used for the calculation of the area as this is the phase in which the monolayer is completely built up. The numerical values of the slopes were determined and assuming k=3·83, the areas were calculated by means of equation 2.

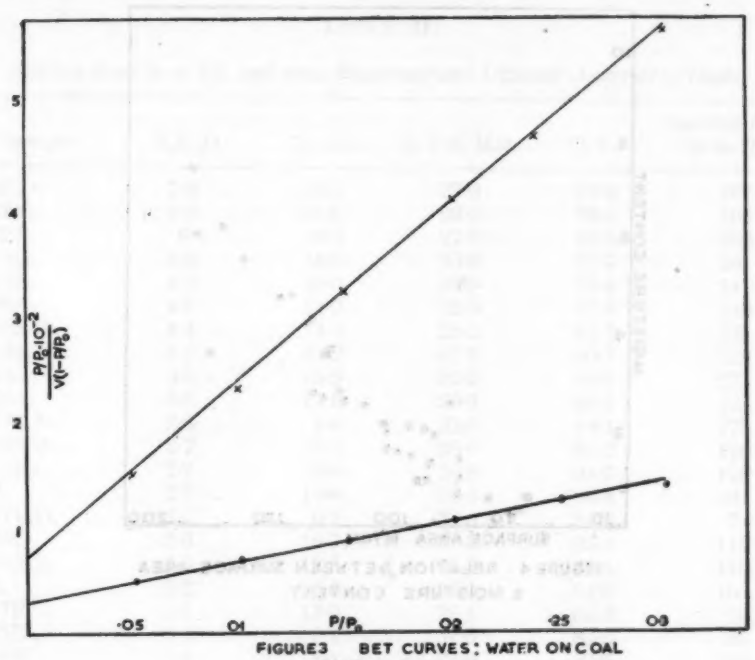

FIGURE 3 BET CURVES: WATER ON COAL
SAMPLE 44C ••••
SAMPLE 268B ××××

Plotting the adsorption data according to the B.E.T. method, straight lines are obtained (Figure 3). The intercept and slope are determined and the monolayer capacity calculated by means of equation 3.

The values of the surface areas as determined by the three methods are given in Table I. The agreement between the values obtained by the B.E.T. and by the Harkins and Jura methods is good. The values determined by the heat of wetting method are higher but still of the same order of magnitude as those calculated from adsorption data.

TABLE I.

Surface Areas Determined by Heat of Wetting, B.E.T. and Harkins and Jura Methods.

Method	Surface Area in cm.^{2}/ g. $\times 10^6$	
	Sample 44C	Sample 268B
Heat of Wetting	0·68	1·41
B.E.T.	0·16	0·72
Harkins and Jura	0·14	1·0

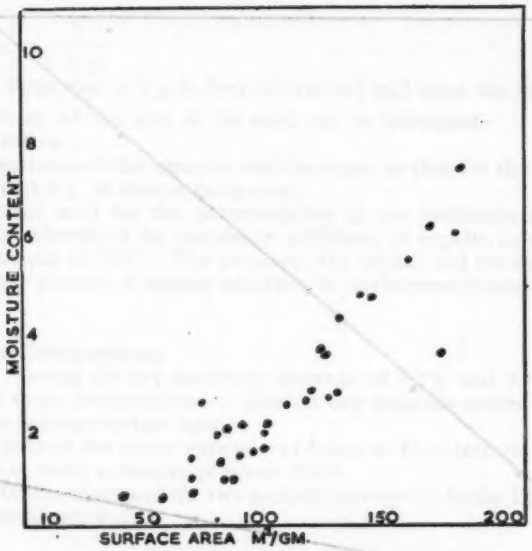

FIGURE 4. RELATION BETWEEN SURFACE AREA & MOISTURE CONTENT

Considering the difficulty of obtaining water adsorption data and the reasonable agreement in values for the surface areas determined by the different methods, it was concluded that the heat of wetting method would be the most practical for this particular investigation, involving, as it does, very many tests. This method was accordingly used to determine the surface area of some thirty typical South African coals.

The results are given in Table II, which also contains data relating to the proximate and ultimate analysis of the coals.

The possibility of a correlation of the surface area with other characteristics of the coal was investigated.

Thus in Figure 4, the relation between the surface area and water content is illustrated. There is a tendency for increase of surface area with increasing moisture content although considerable variation is possible.

A plot of volatile matter content against the surface area shows considerable scatter. The range of volatile matter content considered is not wide enough to give any definite indication of a general trend under these circumstances. The same was found to apply in the case of the carbon content.

TABLE II.

Surface Area in m.²/g. and some Proximate and Ultimate Analysis of Coals.

Sample	%H_2O	% Ash	% Vol. Mat.	% C.	Surface Area in m.²/g.
44C.	7·5	24·2	23·9	78·0	181
22OC.	6·2	23·5	23·0	78·1	165
223P.	6·1	13·3	27·7	81·0	183
224G.	5·6	18·3	33·9	77·7	161
377L.	4·8	18·0	36·8	79·4	141
156A.	4·7	16·9	23·9	82·0	145
158S.W.	4·4	14·4	28·2	80·5	131
113W.	3·7	23·2	41·3	80·1	124
61A.	3·6	15·5	32·3	82·1	175
370A.	3·5	13·0	29·3	83·1	125
157T.N.	2·8	8·6	33·0	84·1	175
328S.W.	2·7	18·2	28·0	81·2	128
272K.	2·7	9·9	29·8	84·7	120
1A.	2·7	14·6	38·8	80·5	131
157V.D.	2·7	9·7	31·0	84·8	74
25A.	2·6	16·7	31·8	85·1	118
250N.S.	2·5	12·5	26·5	84·5	110
8A.	2·2	15·5	36·0	84·0	103
317P.	2·1	13·0	29·4	82·3	90
275Bl.	2·0	9·4	37·5	83·0	85
319W.	1·9	14·4	27·6	82·6	100
323B.	1·8	16·4	27·1	82·6	80
315A.	1·7	9·0	11·6	90·0	156
27G.	1·6	18·8	18·3	84·5	100
21G.	1·5	16·6	35·4	83·2	96
22G.	1·4	14·0	24·4	84·5	70
281Cm.	1·4	14·2	21·2	88·6	90
268B.	1·3	16·8	24·6	88·0	82
446A.	1·0	10·3	18·4	85·5	70
266B.	0·9	11·5	15·5	87·6	84
263Cm.	0·8	15·5	27·6	85·8	85
267B.	0·6	16·1	24·6	85·7	40
271T.	0·6	15·7	26·7	86·5	58
267A.	0·6	15·7	29·4	88·5	70

STRUCTURAL CHANGES IN COAL AT VARIOUS TEMPERATURES.

Not only has Maggs (*loc. cit.*) demonstrated a change in pore structure of coals at low temperatures, but it has also been shown that the rate of penetration of helium at room temperature[17] differs markedly from that of argon at −185°C.[4] The hundred-fold discrepancy between the surface areas determined at room temperature and at −185°C. suggests that more surface is available at higher temperatures and an increase in the rate of penetration may occur.

If this should be the case a considerable rise in temperature will become evident during adsorption of oxygen at temperatures between 70°C. and 100°C. due to the decomposition of peroxygen complexes (formed at lower temperatures with the adsorption of heat[18]) and to the heat liberated by the increased rate of oxygen adsorbed on the new accessible surface.

It was, therefore, decided to obtain some indication of change of availability of surface area and variation of pore diameter with temperature. Following Maggs, it was attempted to obtain nitrogen adsorption data (heat and rate of adsorption and volume adsorbed) at 20°C. and 120°C. At the higher temperature, however, no measureable adsorption takes place and the method was abandoned in favour of a more direct method of following the changes.

This was done by determing the absolute volume of the coal at different temperatures, using helium as a displacement fluid. Volumes were determined at −185°C., −80·5°C., 20°C. and 120°C. Four coals with widely varying moisture contents (1·0 to 7·5%) were used.

For porosity studies the volumes of another seven samples were determined at room temperature.

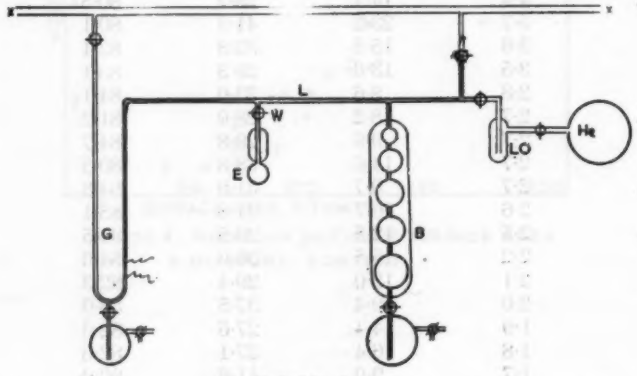

FIGURE 5

The apparatus used is shown schematically in Figure 5. The sample under investigation is in the vessel (E) which is connected to the manifold (L), leading to a constant volume pressure gauge (G), a gas burette (B) and a liquid oxygen trap (LO), through which purified helium may be admitted to the system.

The sample bulb may be at room temperature, like the remainder of the system, or may be maintained at other required temperatures by means of liquid oxygen, solid carbon dioxide or a thermostatically controlled glycerine bath.

The temperatures of the low temperature baths are measured by means of a vapour pressure thermometer.

The volume of the tube connecting sample bulb (E) to the system is kept small in relation to the total capacity of the bulb. This is necessary because its temperature is indeterminable. To reduce the resulting error further, the connecting tube is surrounded by a water jacket.

When taking pressure readings the mercury column in the pressure gauge is always brought to the same reference mark (an electrical contact operating a magic eye was used as an indicator). The pressure is measured by means of a cathetometer.

The volume of the sample bulb at room temperature is obtained by filling the bulb with mercury to the middle of the connecting tube, noting the increase in weight, and calculating the volume from density data.

The total volume of the system, which is equal to the volume of the sample bulb (C_0) and the volume (V_0) of the manifold, is determined by evacuating the system, admitting some helium and determining the pressure when varying the

mercury in the burette in a number of steps, each of known magnitude. (V_1, V_2, V_3 . . . .)

With the total weight of helium in the system equal to G and density ρ_0 at pressure P_0.

$$G=\rho_0 (V_0+C_0)=\rho_0 \frac{P_1}{P_0} (V_0+V_1+C_0)=\rho_0 \frac{P_2}{P_0} (V_0+V_1+V_2+C_0)$$
$$= \ldots \text{ etc.} \qquad (4)$$

from which C_0, V_0, V_1, etc. can be determined. As already indicated C_0 is also determined by direct measurement.

The volume of the manifold (up to stopcock W) is determined in a similar manner.

The volume C_1 of the sample bulb at temperatures other than room temperature is determined by using the equations:—

$$G=\rho_0 V_0+\rho_0{}^1 C_1=\rho_0 V_0+\rho_0 \frac{T_0}{T_1} C_1 \qquad (5)$$

$$G=\rho_1 (V_0+V_1)+\rho_1{}^1 C_1=\rho_0 \frac{P_1}{P_0} (V_0+V_1)+\rho_0 \frac{P_1 T_0}{P_0 T_1} C_1 \qquad (6)$$

In equations (5) and (6) T_1 is the temperature of the bulb, T_0 is the room temperature, $\rho_0{}^1$ the density at the pressure P_0 and temperature T_1 and $\rho_1{}^1$ the density at pressure P_1 and temperature T_1.

The volume of a coal sample is determined by filling the sample bulb with a known mass of coal and evacuating it at 120°C. The coal is assumed to be completely evacuated when, with stopcock 1 closed and the mercury in the manometer at the zero reference contact terminal, no pressure increase is noticeable on the electrical indicator after half an hour. This procedure was necessary because it was found that a reading on the McLeod gauge, while the pumps are running is not necessarily an indication that no more gas is being evolved from the coal.

After evacuation the bulb and its contents are maintained at each of the different temperatures with stopcock (W) closed. Purified helium is admitted and its volume is determined. The stopcock is then slowly opened and the pressures corresponding to the different burette volumes noted after equilibrium has been attained.

The volume of the sample at room temperature is then calculated from sets of equations similar to equation (4).

At the other temperatures the volume is calculated from the following equations (based on equations (5) and (6)).

$$V_0+\frac{T_0}{T_1} (C_1-K_1)=\frac{P_1}{P_0} (V_1+V_0)+\frac{P_1}{P_0} \times \frac{T_0}{T_1} \times (C_1-K_1) \qquad (7)$$

where K_1 is the volume of the sample at temperature T_1.

The determinations are made at four different pressures.

In view of the number of burette steps available, (determining the number of equations in (7)) and the pressure variation, six combinations of results are possible to determine the volume at any of the chosen temperatures.

To determine whether any helium has been adsorbed by the coal at low temperatures (which will of course invalidate the experiments) the total volume of gas (V_T) used for each experiment, and the volume of the gas (V_R) remaining in the manifold (volume V_0) after each burette volume change, were calculated and reduced to N.T.P. If no adsorption takes place the volume entering the bulb (i.e. $V_T-V_R=V_E$) divided by the pressure should be constant at different pressures. Thus:—

$$\frac{V_{E_0}}{P_0}=\frac{V_{E_1}}{P_1}=\frac{V_{E_2}}{P_2}=\text{constant}=N \qquad (8)$$

The values of the constant N were calculated at four different pressures for four coal samples. (The weight of the samples was about 20 g. and the maximum pressure 18 cm. of mercury.)

The results indicated that helium was not adsorbed at —185°C. under the stated conditions.

It was difficult to follow the initial rate of penetration due to the sudden drop in pressure when the gas was admitted to the cold bulb. After about 5 minutes the rate of change of the pressure decreased considerably and equilibrium was attained in about 30 minutes. At higher pressures equilibrium was established in about five minutes. No hysteresis was noticeable when the pressure was again decreased; in most cases the cathetometer reading was exactly reproduced.

The rate of penetration at the higher temperature was much faster, equilibrium being attained within five minutes.

It is, of course, possible that quantities of helium, smaller than the amount measurable by the apparatus, are adsorbed by the coal but it is improbable that such small quantities would affect the measured volumes materially. Dryden[10] states that coal does in fact adsorb helium at —196°C. but gives no experimental data. The "International Critical Tables" quotes values of helium adsorption on wood charcoal but this is not necessarily comparable with coal due to its usually very extensive surface area.

The results of the volume measurements on 10 g. samples at different temperatures are given in Table III. The average of six values obtained at each temperature is given. The maximum deviation between these values is about 1%. Duplicate experiments on the same samples were reproducible to within 1%.

TABLE III.

Measured volumes on 10*g. Samples at Four Temperatures.*

Sample	Air dry Moisture Content	Volume in cc. of 10 g. of coal at			
		—185°C.	—80°C.	20°C.	120°C.
250N.S.	2·5	6·94	6·78	6·82	6·90
272K.	2·7	7·61	7·32	7·09	7·25
44C.	7·5	6·27	6·25	6·44	6·30
268B.	1·3	7·07	6·45	6·75	—
281Cm.	1·4	7·13	6·85	6·94	6·94
220C.	6·2	6·25	6·30	6·40	6·40

The results generally indicate a volume increase at —185°C. as compared to the volume at room temperature. Samples 44C and 220C, however, decreased in volume. This is probably due to the open-structured nature of the two coals, some indication of which is given by their moisture contents (7·5% and 6·2% respectively) and their high heat of wetting values (18·1 cal./g. and 16·5 cal./g.). This is in conformity with the findings of Maggs[9] who demonstrated that the decrease in low temperature nitrogen adsorption is more pronounced in coals with low moisture contents.

The average increase in the measured volume is about 5%. This increase can only be attributed to pore constriction. Bearing in mind that the coal will contract by about 3%[14] for a temperature decrease of 200°C. the real increase in volume is about 8%.

The effect of the increase in volume upon surface area measurements at low temperatures is illustrated by the following considerations. If it is assumed that the increase in volume is brought about by the closing up of pores it is evident that about 8% of the total pore volume becomes inaccessible to the helium molecules, (2 Å in diameter). A rough estimate of the surface area of these pores can be calculated by means of the relationship.

$$r = \frac{2 \times PV}{S} \qquad (9)$$

where r is the radius of the pores, PV the pore volume and S the surface area. Assuming a total pore volume of 0·1 cc./g. the area is about $8{\cdot}0 \times 10^5$ cm.^{2}/g.

This surface area will, in any case, not be available to larger molecules such as those of oxygen and nitrogen, but it is not unreasonable to assume that a similar effect will be produced by pores with larger diameters, depending, however, on the pore size distribution of the coal.

The measured decrease in volume at −80·5°C. is probably due to the simultaneous effect of the contraction of the coal substance and of the constriction of pores. It is possible that the contraction of the coal masks the effect of the pore constriction at this temperature. The volume of sample 272K increased from 7·32 cc. /10 g. at room temperature to 7·09 cc./10 g. at −80·5°C. which might be due to a different pore size distribution.

It was not considered advisable to extend the study to even higher temperatures, where volume changes will be more pronounced, because of the possibility of decompostion of the coal at temperatures higher than 120°C. Volume changes that might be observed at such higher temperatures would therefore be of dubious value.

However, if the volume changes at −185°C. are real, it is possible that a similar phenomenon will manifest itself at high temperatures and this will have a considerable influence on the rate of gas absorption.

THE TRUE DENSITY OF SOUTH AFRICAN COALS.

Wandless and Macrae[19] have shown that there is a relation between the density and the hydrogen content of pure coal. Franklin[20] has extended this work and established that the true density (as determined by helium displacement) is a linear function of the hydrogen content of most coals:

$$\text{Specific volume} = 0{\cdot}043H + 0{\cdot}54 \qquad (10)$$

where H is the hydrogen content. (Mineral-matter-free basis). If the validity of Franklin's equation could be proved for South African coals it would afford a means of calculating the true density of a coal from its proximate and ultimate analysis. This would also be advantageous in porosity studies since the only additional measurement required would be that of the apparent density in a liquid having a large molecular volume.

For the purpose of this study the Parr-formula[21] has been used for the calculation of the percentage mineral matter in coal.

$$\text{Mineral matter} = 1{\cdot}08 \text{ ash} + 0{\cdot}55 \text{ sulphur} \qquad (11)$$

The experimental procedure for the determination of the helium density at room temperature has already been described.

An estimate of the mean specific gravity of the mineral matter is also required to calculate the density of the pure coal substance. This value may be computed by assuming the density of the pyrites to be 5·0 g./cc., and that of the other minerals in the coal 2·7 g./cc.

The specific volume as determined in helium, reduced to a mineral matter-free basis, and the values calculated from the hydrogen content according to Franklin's relation are given in Table IV. The agreement is satisfactory for the series of coals with stated hydrogen content.

TABLE IV.
Specific Volume Calculated from Franklin's Relation and Determined Directly by Helium Displacement.

Sample	% M.M.	% H (D.M.F.)	Specific Volume in cc./g. Determined	Calculated
271T.	18·3	5·15	0·763	0·761
319W.	18·0	4·95	0·748	0·753
272K.	11·6	4·91	0·755	0·751
281Cm.	16·6	4·90	0·862	0·751
263Cm.	18·6	4·84	0·755	0·748
268B.	19·5	4·79	0·753	0·746
266B.	13·5	4·53	0·749	0·735
250N.S.	14·2	4·48	0·733	0·733
44C.	28·8	4·46	0·736	0·732
220C.	27·5	4·45	0·735	0·731
328S.W.	19·3	4·37	0·725	0·728

In the following section this relationship is utilised in conjunction with mercury density determinations to calculate the pore volume of coal.

PORE VOLUME AND PORE SIZE DISTRIBUTION OF COALS.

Porous substances are characterised by certain related quantities, viz. particle density, true density and internal surface area. Having determined the densities, valuable information regarding the pore structure of the substance can be obtained. The most accurate way to determine these densities is by mercury and helium displacement respectively. The difference in specific volume in these two media gives the total pore volume of the material.

The sizes of the pores within a porous material may vary considerably. For convenience, the pores in porous substances are generally classified into micro- and macro-pores, the boundary being 100 Å.

It is possible to calculate a rough value of the average pore radius from the relation between the surface area and the pore volume, assuming cylindrical pores. (Equation 9). From this relationship it is evident that the large pores contribute very little to the total surface area of the material, but their importance as distributing arteries and their influence on diffusion velocities in gas absorption phenomena is obvious.

In processes involving diffusion rates and availability of internal surface, as in the case of oxygen absorption rates by coal, a knowledge of the pore size distribution is important. It is known that the rate of oxygen absorption by coals varies within wide limits. A ratio of ten to one in the absorption rate of two South African coals is not uncommon, while the ratio of the surface area of the same two coals is only about three to one. This is almost certainly due to a difference in pore structure, although the significance of the chemical properties should naturally not be overlooked.

There are several methods for determining the pore size distribution of porous substances. In most of these methods calculations are based on the low temperature adsorption data. Such a procedure does not seem advisable in the case of coal in view of the experimental evidence produced by Maggs (*loc. cit.*) relating to the change in structure of coals at low temperatures. Futhermore, distribution functions can only be determined in the micropore region, as adsorption data at high relative pressures, corresponding to condensation in macro-pores, can only be obtained with difficulty, and extrapolations are uncertain.

The method used in this investigation was based on density determinations by a mercury displacement method devised by Ritter and Drake[12]. Mercury, due to its high surface tension, does not enter into any but the largest pores of a porous substance so that at normal pressure an apparent density is obtained. With increasing pressure the mercury is forced into pores of progressively smaller size. The volume of mercury forced into the coal is measured electrically in a glass dilatometer placed in an autoclave.

The experimental data are represented graphically by plotting the volume of mercury "absorbed" (V) against the applied pressure (P). From this plot the distribution curve is derived as follows: The distribution function D(r) is given by the equation

$$D(r) = \frac{P}{r}\left(\frac{(dV)}{dP}\right) \qquad (12)$$

where r is the pore radius. $\frac{dV}{dP}$ is determined by graphical differentiation at a point on the curve corresponding to a pressure P. The distribution curve is obtained by plotting D(r) against r. The radius r is calculated by means of the relation

$$Pr = 2\phi \cos\theta \qquad (13)$$

where P is the external pressure, ϕ is the surface tension and θ the contact angle between the liquid and the solid.

The contact angle of mercury on coal was measured directly. Measurements were made on enlarged images obtained from photographs of globules of mercury on polished coal surfaces. The average value (145°) of measurements made on six different coals was used for application in equation (13).

The macropore volume was determined at 750 atmospheres corresponding to the pressure, calculated from equation 13, to force mercury into pores of radii greater than 100 Å.

The apparatus is essentially the same as that used by Ritter and Drake (*loc. cit.*) although some modifications have been made. The dilatometer (Figure 6A) has been modified and was also used as a pycnometer for mercury density determinations. The method of filling the dilatometer has also been modified.

From the observations of Ritter and Drake (*loc. cit.*) and Maggs et al.[14] it seemed likely that macroporosity and apparent density of coals would be dependent on the particle size. For comparative purposes it seemed desirable to determine apparent densities on samples of the same particle size (or as near as possible to it) as that of the samples used in other determinations. Samples ground to pass a 60 B.S.S. sieve had been used in all these earlier tests. Because mercury will not penetrate the intergranular spaces of very fine samples a series of density measurements were made on a number of sieve fractions of different coals. The −60+100 mesh fraction, yielded satisfactory results, check values agreeing to within 0·7%. The density and macroporosity measurements were therefore made on this sieve fraction.

In preparing for a test, the dilatometer was charged with about 15 g. of coal and weighed. It was then connected to a high vacuum system and evacuated for 12 hours at a temperature of 120°C.

Figure 6(B) illustrates the apparatus used to fill the dilatometer with mercury after evacuation. With the pumps running the Hoffmann clamp (H) on the connecting tube of the mercury reservoir was slowly released and the mercury was allowed to rise in the connecting tube and eventually to pass through the glass jet (J) and to drop into the dilatometer. When the dilatometer was filled the pumps were stopped and the pressure in the system was increased to about 20 cm. by admitting some air, which resulted in an appreciable drop of the mercury in the capillary. More

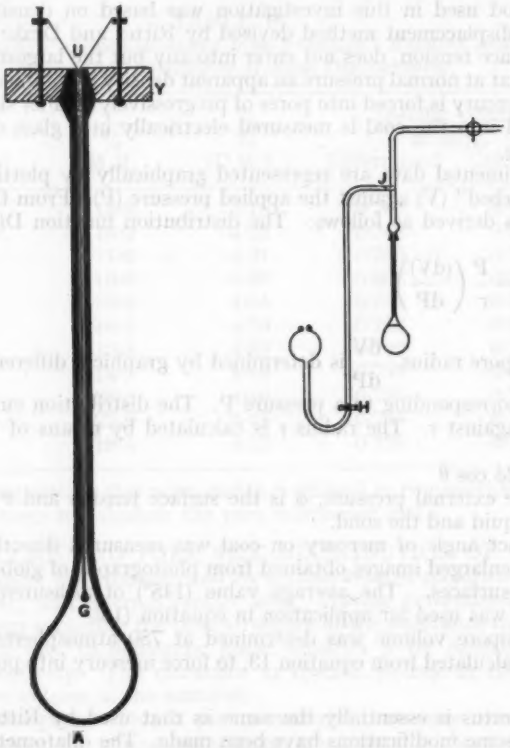

FIGURE 6

mercury was added and the process repeated until the dilatometer was filled (at 25°C. and atmospheric pressure) up to a reference mark on the capillary.

An increase in the pressure to about 30 cm. Hg. above atmospheric did not result in any change in the height of the mercury in the capillary. This leads one to conclude that atmospheric pressure and the pressure exerted by the mercury in the capillary (about 18 cm.) were sufficient to cause the mercury to fill all the intergranular spaces.

The dilatometer was then detached from the high vacuum system and weighed for density determinations. The apparatus was then placed in an autoclave and the volume of mercury forced into the pores of the coal determined at different pressures.

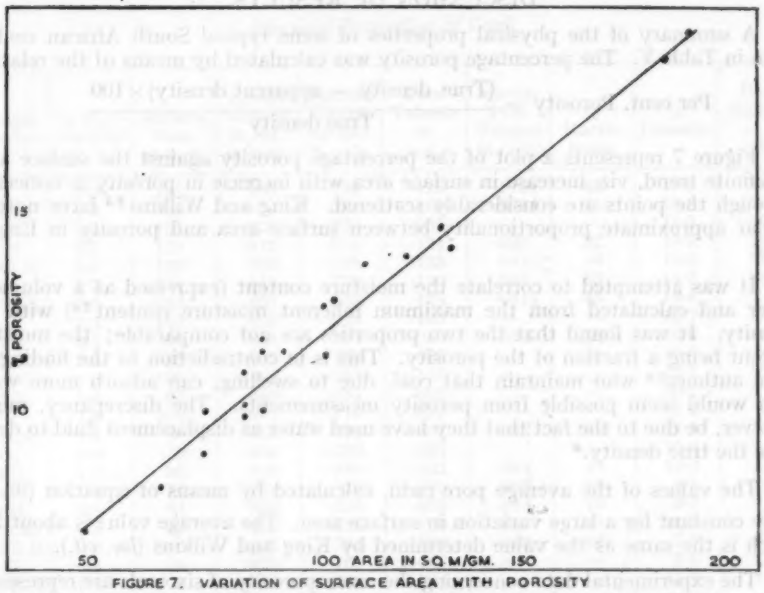

FIGURE 7. VARIATION OF SURFACE AREA WITH POROSITY

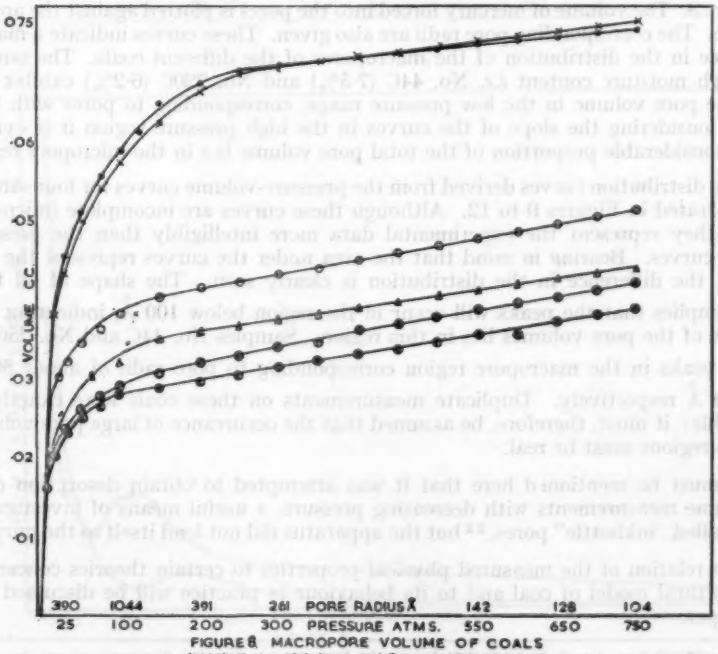

FIGURE 8. MACROPORE VOLUME OF COALS
SAMPLE No. 220C×××, 44C••••, 250NS⊙⊙⊙.
SAMPLE No. 268 B△△△, 328SW⊙⊙⊙, 772K⊙⊙⊙.

DISCUSSION OF RESULTS.

A summary of the physical properties of some typical South African coals is given in Table V. The percentage porosity was calculated by means of the relation:

$$\text{Per cent. Porosity} = \frac{(\text{True density} - \text{apparent density}) \times 100}{\text{True density}}$$

Figure 7 represents a plot of the percentage porosity against the surface area. A definite trend, viz. increase in surface area with increase in porosity is noticeable although the points are considerably scattered. King and Wilkins[23] have noted a similar approximate proportionality between surface area and porosity in English coals.

It was attempted to correlate the moisture content (expressed as a volume of water and calculated from the maximum inherent moisture content[24]) with the porosity. It was found that the two properties are not comparable; the moisture content being a fraction of the porosity. This is in contradiction to the findings of some authors[14] who maintain that coal, due to swelling, can adsorb more water than would seem possible from porosity measurements. The discrepancy, might, however, be due to the fact that they have used water as displacement fluid to determine the true density.*

The values of the average pore radii, calculated by means of equation (9), are fairly constant for a large variation in surface area. The average value is about 20Å which is the same as the value determined by King and Wilkins (*loc. cit.*).

The experimental data concerning the macroporosity of six coals are represented in Figure 8. The volume of mercury forced into the pores is plotted against the applied pressure. The corresponding pore radii are also given. These curves indicate a marked difference in the distribution of the macropores of the different coals. The samples with high moisture content *i.e.* No. 44C (7·5%) and No. 220C (6·2%) exhibit considerable pore volume in the low pressure range, corresponding to pores with large radii. Considering the slope of the curves in the high pressure region it is evident that a considerable proportion of the total pore volume lies in the micropore region.

The distribution curves derived from the pressure-volume curves for four samples are illustrated in Figures 9 to 12. Although these curves are incomplete (micropore region) they represent the experimental data more intelligibly than the pressure-volume curves. Bearing in mind that the area under the curves represent the pore volume, the difference in the distribution is clearly seen. The shape of all these curves implies that the peaks will occur in the region below 100 Å, indicating that the bulk of the pore volumes lies in this region. Samples No. 44C and No. 250N.S. exhibit peaks in the macropore region corresponding to pore radii of about 500 Å and 750 Å respectively. Duplicate measurements on these coals were exactly reproducible; it must, therefore, be assumed that the occurrance of large pore volumes in these regions must be real.

It must be mentioned here that it was attempted to obtain desorption data, *i.e.* volume measurements with decreasing pressure, a useful means of investigating the so-called "inkbottle" pores,[22] but the apparatus did not lend itself to the purpose.

The relation of the measured physical properties to certain theories concerning the structural model of coal and to its behaviour in practice will be discussed in a later paper.

*Franklin,[17] after a detailed study of the methods used for density determinations, has concluded that water, due to poor wettability, is not a suitable displacement fluid.

TABLE V.

Physical Properties of Coal.

Sample Number	% H_2O Air-Dry	Surface Area sq.m/g.	Specific Volume in Hg. in cc/g.	Specific Volume in He. in cc/g.	Pore Volume in cc/g.	Macro-Pore Volume in cc/g.	% Macro-pores	% Porosity	Pore Radius Å
44C.	7·5	181	·908	·732	·176	·0734	42	19·4	19
220C.	6·2	165	·900	·731	·169	·0744	44	18·8	20
224G.	5·6	161	·827	·730	·097	—	—	11·7	12
272K.	2·7	120	·872	·751	·121	·039	32	13·9	20
328S.W.	2·7	128	·853	·728	·125	·042	34	14·6	20
1A.	2·7	131	·840	·720	·120	·064	53	14·2	18
250N.S.	2·5	110	·851	·733	·118	·0511	43	13·8	21
8A.	2·2	103	·828	·723	·105	—	—	12·7	20
317P.	2·1	90	·851	·761	·090	·052	58	10·0	20
275Bl.	2·0	85	·833	·750	·083	—	—	10·0	20
319W.	1·9	100	·863	·753	·110	—	—	12·7	22
323B.	1·8	80	·840	·754	·086	—	—	10·2	21
27G.	1·6	100	·807	·716	·091	—	—	11·2	18
281Cm.	1·4	90	·858	·751	·107	·042	39	12·5	24
22G.	1·4	70	·804	·720	·084	—	—	10·0	22
268B.	1·3	82	·848	·746	·102	·043	42	12·0	25
446A.	1·0	70	·790	·720	·070	·035	50	8·8	20
266B.	0·9	84	·808	·735	·073	·043	59	9·7	21
263Cm.	0·8	85	·850	·750	·100	·041	41	11·8	23
267B.B.	0·6	40	·822	·764	·058	·038	66	7·0	29
271T.	0·6	58	·828	·761	·067	—	—	8·1	23
267B.A.	0·6	79	·856	·762	·094	—	—	11·0	24

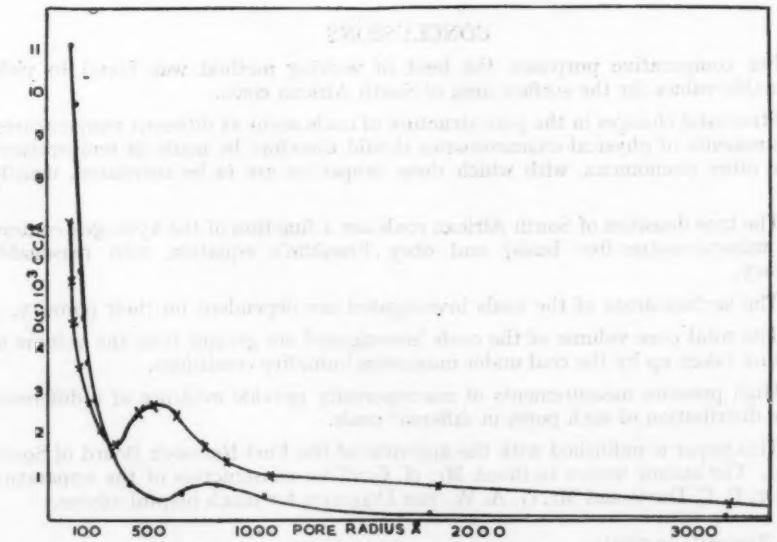

FIGURE 9

DISTRIBUTION CURVES FOR SAMPLES Nos. 250NS(·····) & 44C (———)

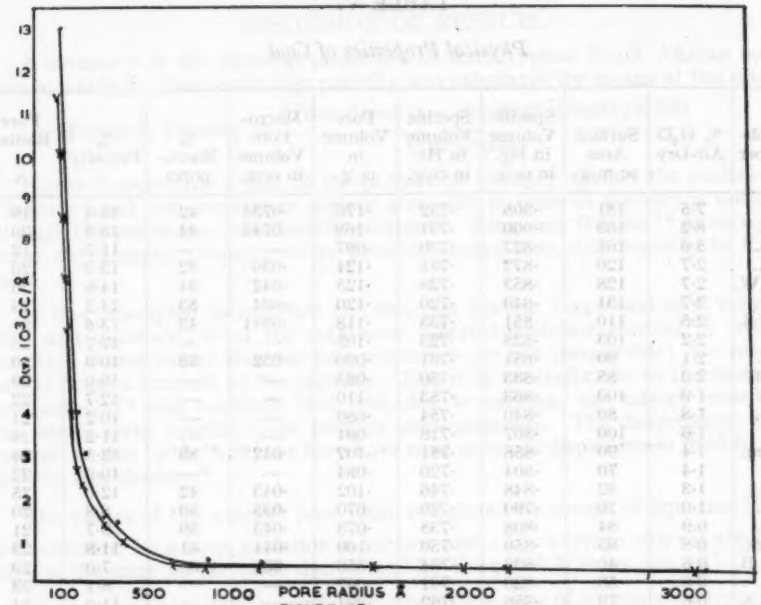

FIGURE. 10
DISTRIBUTION CURVES FOR SAMPLES NoS. 328 SW(••••)& 272K.(xxxx)

CONCLUSIONS

For comparative purposes, the heat of wetting method was found to yield reasonable values for the surface area of South African coals.

Structural changes in the pore structure of coals occur at different temperatures. Measurements of physical characteristics should therefore be made at temperatures where other phenomena, with which these properties are to be correlated, usually occur.

The true densities of South African coals are a function of the hydrogen content (dry mineral-matter-free basis) and obey Franklin's equation with reasonable accuracy.

The surface areas of the coals investigated are dependent on their porosity.

The total pore volume of the coals investigated are greater than the volume of moisture taken up by the coal under maximum humidity conditions.

High pressure measurements of macroporosity provide evidence of a difference in the distribution of such pores in different coals.

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Fuel Research Institute,
Pretoria.

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